PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2006-316287
(43)Date of publication of application : 24.11.2006

(51)Int.Cl. *C08L 101/10 (2006.01)*
C08K 5/5415 (2006.01)

(21)Application number : 2006-239234
(22)Date of filing : 04.09.2006

(71)Applicant : KANEKA CORP
(72)Inventor : OKAMOTO TOSHIHIKO
WAKABAYASHI KATSUO
ITO YASUSHI
ANDO HIROSHI

(30)Priority
Priority number : 2002319335 Priority date : 01.11.2002 Priority country : JP

(54) CURABLE COMPOSITION

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for improving the restorability, durability and creep resistance of a cured product, and to provide a curable composition capable of giving cured products having excellent restorability, durability and creep resistance.
SOLUTION: This method for improving the restorability, durability and creep resistance of the cured product is characterized by using a curable composition containing an organic polymer (A1) having silicon-containing functional groups capable of cross-linking by forming siloxane bonds, wherein the silicon-containing functional groups capable of cross-linking by forming siloxane bonds are silicon-containing functional groups having three or more hydrolysable groups on the silicon.

CLAIMS

[Claim(s)]
[Claim 1]
Stability, endurance, and creep resistance corrective strategy of a hardened material using an organic polymer (A) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and a hardenability constituent containing silicate (B).
[Claim 2]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, Stability, endurance, and creep resistance corrective strategy of a hardened material, wherein a silicon containing functional group which can construct a bridge by forming a siloxane bond uses on silicon a hardenability constituent containing an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases.
[Claim 3]
A main chain of an organic polymer (A1) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, Stability, endurance, and creep resistance corrective strategy of the hardened material according to claim 2 using a hardenability constituent which is an acrylic ester system copolymer manufactured by a living-radical-polymerization method (meta).
[Claim 4]
Stability, endurance, and creep resistance corrective strategy of the hardened material according to claim 2 or 3 using a hardenability constituent which contains silicate (B) further.
[Claim 5]
Stability, endurance, and creep resistance corrective strategy of the hardened material according to any one of claims 2 to 4 using a hardenability constituent which contains carboxylic acid tin salt (C) further.
[Claim 6]
Stability, endurance, and creep resistance corrective strategy of the hardened material according to any one of claims 2 to 5 using a hardenability constituent which contains an organic tin catalyst (D) further.
[Claim 7]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, Stability, endurance, and creep resistance corrective strategy of a hardened material using a hardenability constituent which is an organic polymer (A2) which averages per molecule a silicon containing functional group over which this organic polymer can construct a bridge by forming a siloxane bond, and has it 1.7-5 pieces.
[Claim 8]
Stability, endurance, and creep resistance corrective strategy of the hardened material according to claim 7, wherein a silicon containing functional group which can construct a bridge by forming a siloxane bond uses on silicon a hardenability constituent which is a silicon containing functional group which has three or more hydrolytic bases.
[Claim 9]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond introduced an unsaturation group into an end, and a general formula (1) :

$H-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (1)

an alkyl group of the carbon numbers 1-20 from which R^1 in a formula and R^2 were the same as or different. When the Tori ORGANO alloxy group shown by aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or $(R')_3SiO-$ is shown and R^1 or two or more R^2 exist, they may be the same and may differ. R' is a hydrocarbon group of monovalence of the carbon numbers 1-20 here, and three R' may be the same and may differ. X shows a hydroxyl group or a hydrolytic basis, and when two or more X exists, they may be the same and may differ. As for a, 0, 1, 2, or 3b shows 0, 1, or 2, respectively. About b in m bases ($SiR^1_{2-b}X_bO$), they may be the same and may differ. m shows an integer of 0 to 19. however -- what satisfies a+sigma b>=1 -- carrying out -- the stability of the hardened material according to claim 1 or 7 using a hardenability constituent which is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed, endurance, and creep resistance corrective strategy.
[Claim 10]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond introduced an unsaturation group into an end, and a general formula (2) :
$H-SiX_3$ (2)

(X in a formula shows a hydroxyl group or a hydrolytic basis, and three X may be the same and) It may differ. Stability, endurance, and creep resistance corrective strategy of a hardened material given in either [Claims 2, 3, 4 and 5 using a hardenability constituent which is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed, and] 6 or 8.
[Claim 11]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and this organic polymer is a general formula (3). :
$-O-R^3-CH(CH_3)-CH_2-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (3)

(R^3 in a formula a divalent organic group of the carbon numbers 1-20 which contain one or more sorts chosen from a group which consists of hydrogen, oxygen, and nitrogen as a composition atom) [show and] R^1, R^2, X, a, b, and m -- the above -- it is the same -- the stability of a hardened material using a hardenability constituent which is an organic polymer (A3) which has a structure part with which it is expressed, endurance, and creep resistance corrective strategy.
[Claim 12]
An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (4). :
$-O-R^3-C(CH_3)=CH_2$ (4)

An organic polymer which introduced an unsaturation group expressed with (R^3 is the same as the above), and a general formula (1) :
$H-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (1)

Stability, endurance, and creep resistance corrective strategy of the hardened material according to claim 11 using a hardenability constituent which is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (R^1 in a formula, R^2, X, a, b, and m are the same as the above).
[Claim 13]
An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (5). :
$-O-R^3-CH(CH_3)-CH_2-SiX_3$ (5)

(R^3 in a formula and X are the same as the above.) -- the stability of the hardened material according to claim 11 or 12 using a hardenability constituent which is an organic polymer which has a structure part with which it is expressed, endurance, and creep resistance corrective strategy.
[Claim 14]
An organic polymer which has a silicon containing functional group which can construct a bridge by

forming a siloxane bond, Stability, endurance, and creep resistance corrective strategy of the hardened material according to any one of claims 1 to 13 using for a principal chain skeleton a hardenability constituent which is an organic polymer which does not contain an amide segment (−NH−CO−) substantially.
[Claim 15]
A silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

(three R^4 is the organic groups of monovalence of the carbon numbers 2–20 independently among a formula, respectively.) — the stability of the hardened material according to any one of claims 1 to 14 using a hardenability constituent which is a basis expressed, endurance, and creep resistance corrective strategy.
[Claim 16]
Stability, endurance, and creep resistance corrective strategy of the hardened material according to any one of claims 1 to 15, wherein a silicon containing functional group which can construct a bridge by forming a siloxane bond uses a hardenability constituent which is a triethoxy silyl group.
[Claim 17]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, Thin layer hardenability corrective strategy, wherein a silicon containing functional group which can construct a bridge by forming a siloxane bond uses on silicon an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases, and a hardenability constituent containing an organic tin catalyst (D).
[Claim 18]
An organic polymer (A) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, And adhesives for interior panels containing silicate (B), Adhesives for face panels, adhesives for tiling, adhesives for stone tensions, ceiling finishing adhesives, Floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, the electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 19]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, A silicon containing functional group which can construct a bridge by forming a siloxane bond, . It is characterized by containing an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 20]
A main chain of an organic polymer (A1) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, Using a hardenability constituent which is an acrylic ester system copolymer manufactured by a living−radical−polymerization method (meta) to Claim 19 by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 21]
Claim 19 containing silicate (B) further or 20 descriptions, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing

material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 22]
From Claim 19 containing carboxylic acid tin salt (C) further, to either of 21 A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 23]
From Claim 19 containing an organic tin catalyst (D) further, to either of 22 A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 24]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, It is characterized by this organic polymer being an organic polymer (A2) which averages per molecule a silicon containing functional group which can construct a bridge by forming a siloxane bond, and has it 1.7–5 pieces. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 25]
A silicon containing functional group which can construct a bridge by forming a siloxane bond, The Claim 24 description being a silicon containing functional group which has three or more hydrolytic bases on silicon, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 26]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond introduced an unsaturation group into an end, and a general formula (1) :

$H-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (1)

That it is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (R^1 in a formula, R^2, X, a, b, and m are the same as the above) to Claim 18 by which it is characterized, or 24 A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision−mechanical−equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.
[Claim 27]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond introduced an unsaturation group into an end, and a general formula (2) :

H-SiX_a (2)

That it is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (X in a formula is the same as the above) to either [Claims 19, 20, 21 and 22 by which it is characterized, and] 23 or 25 A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 28]

It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and this organic polymer is a general formula (3). :

$-O-R^3-CH(CH_3)-CH_2-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (3)

. It is characterized by being an organic polymer (A3) which has a structure part expressed with (R^1 in a formula, R^2, R^3, X, a, b, and m are the same as the above). Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 29]

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (4). :

$-O-R^1-O(CH_3)=CH_2$ (4)

An organic polymer which introduced an unsaturation group expressed with (R^1 is the same as the above), and a general formula (1) :

H-$(SiR^2_{2-b}X_bO)_m$-$SiR^2_{3-a}X_a$ (1)

That it is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (R^2 in a formula, R^3, X, a, b, and m are the same as the above) to Claim 28 by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 30]

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (5). :

$-O-R^1-CH(CH_3)-CH_2-SiX_3$ (5)

(R^1 in a formula and X are the same as the above.) — it is characterized by being an organic polymer which has a structure part with which it is expressed — being according to claim 28 or 29, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 31]

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, From Claim 18 being an organic polymer which does not contain an amide segment (-NH-CO-) substantially in a principal chain skeleton, to either of 30 A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone

tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 32]

A silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

(R^4 in a formula is the same as the above.) — it is characterized by being a basis expressed — being according to any one of claims 18 to 31, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 33]

A silicon containing functional group which can construct a bridge by forming a siloxane bond, From Claim 18 being a triethoxy silyl group, to either of 32 A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, The electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[Claim 34]

It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, An organic polymer (A1) whose silicon containing functional group which can construct a bridge by forming a siloxane bond is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing silicate (B).

[Claim 35]

The hardenability constituent according to claim 34, wherein silicate is a condensate of tetra alkoxysilane.

[Claim 36]

It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, A silicon containing functional group which can construct a bridge by forming a siloxane bond, An organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing carboxylic acid tin salt (C1) whose carbon of an alpha position of a carboxyl group is the 4th class carbon.

[Claim 37]

It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, An organic polymer (A1) and carboxylic acid tin salt (C) whose silicon containing functional group which can construct a bridge by forming a siloxane bond is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing an organic tin catalyst (D).

[Claim 38]

It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, An organic polymer (A1) whose silicon containing functional group which can construct a bridge by forming a siloxane bond is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing a non-tin catalyst (E).

[Claim 39]

It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, An organic polymer (A1) whose silicon containing functional group which can construct a bridge by forming a siloxane bond is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing a minute hollow

body (F).
[Claim 40]
It is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, A silicon containing functional group which can construct a bridge by forming a siloxane bond, A hardenability constituent, wherein it is a hardenability constituent containing an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon and this organic polymer is 5 to 28 % of the weight in a total amount of a hardenability constituent.
[Claim 41]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond introduced an unsaturation group into an end, and a general formula (2) :
H-SiX$_3$ (2)

The hardenability constituent according to any one of claims 34 to 40 being an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (X in a formula is the same as the above).
[Claim 42]
A silicon containing functional group which can construct a bridge by forming a siloxana bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

The hardenability constituent according to any one of claims 34 to 41 being a basis expressed with (R^4 in a formula is the same as the above).
[Claim 43]
A silicon containing functional group which is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and can construct a bridge by forming a siloxane bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

An organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above), and a general formula (7) :
- SiR^5_c(OR^6)$_{3-c}$ (7)

(c R^5 is the organic groups of monovalence of the carbon numbers 1-20 independently among a formula, respectively.)
3-c R^6 is the organic groups of monovalence of the carbon numbers 2-20 independently, respectively, and c shows 0, 1, or 2. A hardenability constituent in which storage stability containing an aminosilane coupling agent (G) which has a basis expressed has been improved.

[Claim 44]
A silicon containing functional group which is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and can construct a bridge by forming a siloxane bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

An organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above), and a general formula (8) :
- SiR^7_d(OCH$_3$)$_e$(OR^8)$_{3-d-e}$ (8)

(d R^7 is the organic groups of monovalence of the carbon numbers 1-20 independently among a formula, respectively.)
It is an organic group of monovalence of the carbon numbers 2-20 independently, and d shows 0, 1, or 2 and, as for R^8 of a 3-d-e individual, e shows 1, 2, or 3, respectively.
However, 3-d-e>=0 shall be satisfied. A hardenability constituent in which it is a hardenability constituent containing an aminosilane coupling agent (H) which has a basis expressed, and a cure rate recuperating onoself beforehand in this hardenability constituent has been improved.

[Claim 45]
A silicon containing functional group which is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and can construct a bridge by forming a siloxane bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

An organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above), and a hardenability constituent containing epoxy resin (I).
[Claim 46]
A silicon containing functional group which is a polyoxyalkylene series polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and can construct a bridge by forming a siloxane bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

A polyoxyalkylene series polymer (A5) which has a basis expressed with (R^4 in a formula is the same as the above), And a hardenability constituent containing an acrylic ester system copolymer (A6) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond (meta).
[Claim 47]
A silicon containing functional group which is a saturated hydrocarbon system polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and can construct a bridge by forming a siloxane bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

A hardenability constituent containing a saturated hydrocarbon system polymer (A7) which has a basis expressed with (R^4 in a formula is the same as the above).
[Claim 48]
A silicon containing functional group which is an acrylic ester system copolymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond (meta), and can construct a bridge by forming a siloxane bond is a general formula (6). :
- Si(OR^4)$_3$ (6)

a hardenability constituent containing an acrylic ester system copolymer (A8) which has a basis expressed with (R^4 in a formula is the same as the above) (meta-).
[Claim 49]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond introduced an unsaturation group into an end, and a general formula (9) :
H-Si(OR^4)$_3$ (9)

The hardenability constituent according to any one of claims 42 to 48 being an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (being the same as R^4 above in a formula).
[Claim 50]
The hardenability constituent according to any one of claims 34 to 49 in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond is characterized by being an organic polymer which does not contain an amide segment (-NH-CO-) substantially in a principal chain skeleton.
[Claim 51]
The hardenability constituent according to any one of claims 34 to 50, wherein a silicon containing functional group which can construct a bridge by forming a siloxane bond is a triethoxy silyl group.
[Claim 52]
A silicon containing functional group which is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond, and can construct a bridge by forming a siloxane bond is a ganeral formula (6). :
- Si(OR^4)$_3$ (6)

A general formula (10) carrying out the ester exchange reaction of the compound (J) which has at least one methoxy group which can carry out an ester exchange reaction to an organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above) :

$-Si(OCH_3)_f(OR^4)_{3-f}$ (10)

(3-f R^4 is the organic groups of monovalence of the carbon numbers 2-20 independently among a formula, respectively.)

f shows 1, 2, or 3. A manufacturing method of an organic polymer which has a basis expressed.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]
[0001]
This invention relates to the hardenability constituent containing the organic polymer which has a silicon containing functional group (henceforth a reactive silicon group) which can construct a bridge by forming a siloxane bond.
[Background of the Invention]
[0002]
It is known that the organic polymer which contains at least one reactive silicon group in a molecule has the interesting character in which construct a bridge by formation of the siloxane bond accompanied by the hydrolysis reaction of a reactive silicon group, etc., and a rubber-like hardened material is obtained with hygroscopic surface moisture etc. also in a room temperature.
[0003]
In the polymer which has these reactive silicon groups, a polyoxyalkylene series polymer and a polyisobutylene system polymer are already produced industrially, and are widely used for uses, such as a sealing material, adhesives, and a paint.
[0004]
The adhesives for interior panels, the adhesives for face panels, the adhesives for tiling, the adhesives for stone tensions, When the resin for adhesives used for the adhesives for finishing of wall, the adhesives for car panels, etc. is inferior to stability or creep resistance, an adhesives layer may pass with prudence and the stress from the outside of adherend, it may change by the time, and a panel tile, a stone, etc. may shift. Also in ceiling finishing adhesives or floor finishing adhesives, if inferior to stability or creep resistance, an adhesives layer may pass and it may change by the time, and unevenness of a ceiling surface or a floor line may arise. If the stability of the electrical and electric equipment, an electron, and the adhesives for precision-mechanical-equipment assemblies and creep resistance are bad, an adhesives layer may pass, and it may change by the time, and may be connected with the degradation of apparatus. Therefore, it is called for that the constituent for these adhesives is excellent in stability or creep resistance.
[0005]
A sealing material generally fills up the joined part and crevice between various members, and he is used in order to give watertight and airtightness. Therefore, since the flattery nature to the use part over a long period of time is very important, excelling in stability or endurance is called for as physical properties of a hardened material. Working joint of a building with an especially large change of joint width (Kasagi) the circumference of glass, the circumference of a window frame and a sash, a curtain wall, and various face panels — business — stability and endurance excellent in the constituent used for a sealing material, the sealing material for direct grazing, the sealing material for multiple glass, the sealing material for speed signal generator construction methods, etc. are called for.
[0006]
On the other hand, (the patent documents 1), the (patent documents 2), the (patent documents 3), the (patent documents 4), (The patent documents 5), the (patent documents 6), the (patent documents 7), the (patent documents 8), (The patent documents 9), the (patent documents 10), the (patent documents 11), the (patent documents 12), (The patent documents 13), the (patent documents 14), the (patent documents 15), the (patent documents 16), (The patent documents 17),

the (patent documents 18), the (patent documents 19), the (patent documents 20), In (the patent documents 21), the (patent documents 22), the (patent documents 23), the (patent documents 24), the (patent documents 25), the (patent documents 26), the (patent documents 27), the (patent documents 28), and the (patent documents 29), Although the room-temperature-curing natura constituent which uses as an essential ingredient the organic polymer which has the reactive silicon group which three hydrolytic bases combined on silicon is indicated, In these advanced technology, the fast curability based on the reactive silicon group which three hydrolytic bases combined is mainly indicated, and the description which suggests stability, creep resistance, and endurance is not indicated.
[Patent documents 1] JP,H10-245482,A
[Patent documents 2] JP,H10-245484,A
[Patent documents 3] JP,H10-251552,A
[Patent documents 4] JP,H10-324793,A
[Patent documents 5] JP,H10-330630,A
[Patent documents 6] JP,H11-12473,A
[Patent documents 7] JP,H11-12480,A
[Patent documents 8] JP,H11-21463,A
[Patent documents 9] JP,H11-29713,A
[Patent documents 10] JP,H11-49969,A
[Patent documents 11] JP,H11-49970,A
[Patent documents 12] JP,H11-116831,A
[Patent documents 13] JP,H11-124509,A
[Patent documents 14] WO No. 47939 [98 to]
[Patent documents 15] JP,2000-34391,A
[Patent documents 16] JP,2000-109676,A
[Patent documents 17] JP,2000-109677,A
[Patent documents 18] JP,2000-109678,A
[Patent documents 19] JP,2000-129126,A
[Patent documents 20] JP,2000-129145,A
[Patent documents 21] JP,2000-129146,A
[Patent documents 22] JP,2000-129147,A
[Patent documents 23] JP,2000-136312,A
[Patent documents 24] JP,2000-136313,A
[Patent documents 25] JP,2000-239338,A
[Patent documents 26] JP,2001-55503,A
[Patent documents 27] JP,2001-72854,A
[Patent documents 28] JP,2001-72855,A
[Patent documents 29] JP,2000-327771,A
[Description of the Invention]
[Problem(s) to be Solved by the Invention]
[0007]
An object in view of the above-mentioned actual condition of this invention is to provide the stability, endurance, and creep resistance corrective strategy of a hardened material. The adhesives for interior panels with which stability, endurance, and creep resistance have been improved as for this invention, The adhesives for face panels, the adhesives for tiling, the adhesives for stone tensions, ceiling finishing adhesives, Floor finishing adhesives, the adhesives for finishing of wall, the adhesives for car panels, the electrical and electric equipment, an electron and the adhesives for precision-mechanical-equipment assemblies, It aims at providing the sealing material for direct grazing, the sealing material for multiple glass, the sealing material for speed signal generator construction methods, or the sealing material for working joint of a building. An object of this invention is to provide the hardenability constituent which can give the hardened material excellent in stability, endurance, and creep resistance.
[Means for Solving the Problem]
[0008]
By using on silicon a silicon containing functional group which has three or more hydrolytic basas as

a reactive silicon group of this polymer, as a result of inquiring wholeheartedly, in order that this invention persona may solve such a problem, It found out improving stability, endurance, and creep resistance, and this invention was completed.
[0009]
That is, the 1st is related with stability, andurance, and creep resistance corrective strategy of a hardened material using an organic polymer (A) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and a hardenability constituent containing silicate (B).
[0010]
The 2nd is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond, It is related with stability, endurance, and creep resistance corrective strategy of a hardened material using on silicon a hardenability constituent containing an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases.
[0011]
A main chain of an organic polymer (A1) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment. It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in the above using a hardenability constituent which is an acrylic eater system copolymer manufactured by a living-radical-polymerization method (meta).
[0012]
It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which contains silicate (B) further as a desirable embodiment.
[0013]
It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which contains carboxylic acid tin salt (C) further as a desirable embodiment.
[0014]
It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which contains an organic tin catalyst (D) further as a desirable embodiment.
[0015]
The 3rd is an organic polymer which has a silicon containing functional group which can oonstruct a bridge by forming a siloxane bond of this invention, This organic polymer is related with stability, endurance, and creep resistance corrective strategy of a hardened material using a hardenability constituent which is an organic polymer (A2) which averages par molecule a silicon containing functional group which can construct a bridge by forming a siloxane bond, and has it 1.7-5 pieces.
[0016]
A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment. It related with stability, endurance, and creep resistance corrective strategy of a hardened material given in the above using on silicon a hardenability constituent which is a silicon containing functional group which has three or more hydrolytic bases.
[0017]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment introduced an unsaturation group into an end, and general formula (1) :

$$H-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a \quad (1)$$

an alkyl group of the carbon numbers 1-20 from which R^1 in a formula and R^2 were the same as or different. When the Tori ORGANO siloxy group shown by aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or $(R')_3SiO-$ is shown and R^1 or two or more R^2 exist, they may be the same and may differ. R' is a hydrocarbon group of monovalence of the carbon numbers 1-20 here, and three R' may be the same and may differ. X shows a hydroxyl group or a

hydrolytic basis, and when two or more X exists, they may be the same and may differ. As for a, 0, 1, 2, or 3b shows 0, 1, or 2, respectively. About b in m bases ($SiR^1_{2-b}X_bO$), they may be the same and may differ. m shows an integar of 0 to 19, however -- what satisfies a+sigma b>=1 -- carrying out -- it is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed.
[0018]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment introduced an unsaturation group into an end, and general formula (2) :

$$H-SiX_3 \quad (2)$$

(X in a formula shows a hydroxyl group or a hydrolytic basis. and three X may be the same and) It may differ. It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed.
[0019]
The 4th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and this organic polymer is a general formula (3). :

$$-O-R^3-CH(CH_3)-CH_2-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a \quad (3)$$

(R^3 in a formula a divalent organic group of the carbon numbers 1-20 which contain one or more sorts chosen from a group which consists of hydrogen, oxygen, and nitrogen as a composition atom) [show and] R^1, R^2, X, a, b, and m -- the above -- it is the same -- it is related with stability, endurance, and creep resistance corrective strategy of a hardened material using a hardenability constituent which is an organic polymer (A3) which has a structure part with which it is expressed.
[0020]
An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (4). :

$$-O-R^3-C(CH_3)=CH_2 \quad (4)$$

An organic polymer which introduced an unsaturation group expressed with (R^3 is the same as the above), and general formula (1) :

$$H-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a \quad (1)$$

It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in the above using a hardenability constituent which is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (R^1 in a formula, R^2, X, a, b, and m are the same as the above).
[0021]
An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (5). :

$$-O-R^3-CH(CH_3)-CH_2-SiX_3 \quad (5)$$

(R^3 in a formula and X are the same as the above.) -- it is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which is an organic polymer which has a structure part with which it is expressed.
[0022]
An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment, It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using for a principal chain skeleton a hardenability constituent which is an organic polymer which does not contain an amide segment (-NH-CO-) substantially.
[0023]
A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (6). :

- $Si(OR^4)_3$ (6)

(three R^4 is the organic groups of monovalence of the carbon numbers 2-20 independantly among a formula, respectively.) — it is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either using a hardenability constituent which is a basis expressed.

[0024]

It is related with stability, endurance, and creep resistance corrective strategy of a hardened material given in said either, wherein a silicon containing functional group which can construct a bridge by forming a siloxane bond uses a hardenability constituent which is a triethoxy silyl group as a desirable embodiment.

[0025]

The 5th is an organic polymer which has a silicon containing functional group which can constructa bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond is related with thin layer hardenability corrective strategy using on silicon an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases, and a hardenability constituent containing an organic tin catalyst (D).

[0026]

An organic polymer (A) which has a silicon containing functional group which can construct a bridge when the 6th forms a siloxane bond of this invention, And adhesives for interior panels containing silicate (B), Adhesives for face panels, adhesives for tiling, adhesives for stone tensions, ceiling finishing adhesives, It is related with floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0027]

The 7th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond, . It is characterized by containing an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0028]

A main chain of an organic polymer (A1) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment, Using a hardenability constituent which is an acrylic ester system copolymer manufactured by a living-radical-polymerization method (meta) to the above by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0029]

As a desirable embodiment, containing silicate (B) further to said either by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0030]

As a desirable embodiment, containing carboxylic acid tin salt (C) further to said either by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0031]

As a desirable embodiment, containing an organic tin catalyst (D) further to said either by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0032]

The 8th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention. . It is characterized by this organic polymer baing an organic polymer (A2) which averages per molecule a silicon containing functional group which can construct a bridge by forming a siloxane bond, and has it 1.7-5 pieces. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0033]

A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment, That it is a silicon containing functional group which has three or more hydrolytic bases on silicon to the above by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0034]

An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment introduced an unsaturation group into an end and a general formula (1) :

$$H-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a \quad (1)$$

That it is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (R^1 in a formula, R^2, X, a, b, and m are the same as the above) to said either by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0035]

An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment introduced an unsaturation group into an end and a general formula (2) :

$H-SiX_3$ (2)

That it is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (X in a formula is the same as the above) to said either by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0036]

The 9th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and this organic polymer is a general formula (3). :

$-O-R^3-CH(CH_3)-CH_2-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (3)

. It is characterized by being an organic polymer (A3) which has a structure part expressed with (R^1 in a formula, R^2, R^3, X, a, b, and m are the same as the above). Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0037]

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (4). :

$-O-R^1-C(CH_3)=CH_2$ (4)

An organic polymer which introduced an unsaturation group expressed with (R^1 is the same as the above), and general formula (1) :

$H-(SiR^2_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (1)

That it is an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (R^2 in a formula, R^3, X, a, b, and m are the same as the above) to the above by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0038]

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (5). :

$-O-R^1-CH(CH_3)-CH_2-SiX_3$ (5)

(R^1 in a formula and X are the same as the above.) — a description to said either being an organic polymer which has a structure part with which it is expressed. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0039]

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment, That it is an organic polymer which does not contain an amide segment (-NH-CO-) substantially in a principal chain skeleton to said either by

which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0040]

A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (6). :

$-Si(OR^4)_3$ (6)

(R^4 in a formula is the same as the above.) — a description to said either being a basis expressed. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0041]

A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment, That it is a triethoxy silyl group to said either by which it is characterized A description, Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is related with the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building.

[0042]

The 10th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond is related with an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing silicate (B).

[0043]

As a desirable embodiment, silicate is related with a hardenability constituent given in the above being a condensate of tetra alkoxysilane.

[0044]

The 11th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond, It is related with an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing carboxylic acid tin salt (C1) whose carbon of an alpha position of a carboxyl group is the 4th class carbon.

[0045]

The 12th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond is related with an organic polymer (A1) and carboxylic acid tin salt (C) which are the silicon containing functional groups which have three or more hydrolytic bases on silicon, and a hardenability constituent containing an organic tin catalyst (D).

[0046]

The 13th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond is related with an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing a non-tin catalyst (E).

[0047]

The 14th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond is related with an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon, and a hardenability constituent containing a minute hollow body (F).
[0048]
The 15th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, A silicon containing functional group which can construct a bridge by forming a siloxane bond, It is a hardenability constituent containing an organic polymer (A1) which is a silicon containing functional group which has three or more hydrolytic bases on silicon, and is related with a hardenability constituent, wherein this organic polymer is 5 to 28 % of the weight in a total amount of a hardenability constituent.
[0049]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment introduced an unsaturation group into an end, and general formula (2) :

$H\text{-}SiX_3$ (2)

It is related with a hardenability constituent given in said either being an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (X in a formula is the same as the above).
[0050]
A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (6). :

$-Si(OR^4)_3$ (6)

It is related with a hardenability constituent given in said either being a basis expressed with (R^4 in a formula is the same as the above).
[0051]
A silicon containing functional group which the 16th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

An organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above), and general formula (7) :

$-SiR^5_a(OR^6)_{3-a}$ (7)

(Among a formula, a R^5 is the organic groups of monovalence of the carbon numbers 1-20 independently, and 3-a R^6, respectively) It is an organic group of monovalence of the carbon numbers 2-20 independently, and a shows 0, 1, or 2, respectively. It is related with a hardenability constituent in which storage stability containing an aminosilane coupling agent (G) which has a basis expressed has been improved.
[0052]
A silicon containing functional group which the 17th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

An organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above), and general formula (8) :

$-SiR^7_d(OCH_2)_e(OR^8)_{3-d-e}$ (8)

(Among a formula, d R^7 is the organic groups of monovalence of the carbon numbers 1-20 indapendently, respectively, R^8 of a 3-d-e individual is an organic group of monovalence of the carbon numbers 2-20 independently, and d shows 0, 1, or 2 and, as for e, it shows 1, 2, or 3, respectively.) However, 3-d-e>=0 shall be satisfied. It is a hardenability constituent containing an

aminosilane coupling agent (H) which has a basis expressed, and is related with a hardenability constituent in which a cure rate recuperating oneself beforehand in this hardenability constituent has been improved.
[0053]
A silicon containing functional group which the 18th is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

It is related with an organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above), and a hardenability constituent containing epoxy resin (I).
[0054]
A silicon containing functional group which the 19th is a polyoxyalkylene series polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

A polyoxyalkylene series polymer (A5) which has a basis expressed with (R^4 in a formula is the same as the above). And it is related with a hardenability constituent containing an acrylic ester system copolymer (A6) which has a silicon containing functional group which can construct a bridge by forming a siloxane bond (meta).
[0055]
A silicon containing functional group which the 20th is a saturated hydrocarbon system polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

It is related with a hardenability constituent containing a saturated hydrocarbon system polymer (A7) which has a basis expressed with (R^4 in a formula is the same as the above).
[0056]
The 21st is an acrylic ester system copolymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention (meta), A silicon containing functional group which can construct a bridge by forming a siloxane bond is general formula (6).-Si $(OR^4)_3$ (6).

It is related with a hardenability constituent containing an acrylic ester system copolymer (A8) which has a basis expressed with (R^4 in a formula is the same as the above) (meta-).
[0057]
An organic polymer in which an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment introduced an unsaturation group into an end, and general formula (9) :

$H\text{-}Si(OR^4)_3$ (9)

It is related with a hardenability constituent given in said either being an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (being the same as R^4 above in a formula).
[0058]
An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment, It is related with a hardenability constituent given in said either being an organic polymer which does not contain an amide segment (-NH-CO-) substantially in a principal chain skeleton.
[0059]
A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is related with a hardenability constituent given in said either being a triethoxy silyl group.
[0060]

A silicon containing functional group which the 22nd is an organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond of this invention, and can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

General formula (10) carrying out the ester exchange reaction of the compound (J) which has at least one methoxy group which can carry out an ester exchange reaction to an organic polymer (A4) which has a basis expressed with (R^4 in a formula is the same as the above) :

$-Si(OCH_3)_{3-f}(OR^4)_f$ (10)

(among a formula, 3-f R^4 is the organic groups of monovalence of the carbon numbers 2-20 independently, respectively, and f shows 1, 2, or 3.) — it is related with a manufacturing method of an organic polymer which has a basis expressed.

[0061]

Hereafter, this invention is explained in detail.

[0062]

Restriction in particular does not have a principal chain skeleton of an organic polymer (A) which has a reactive silicon group used for this invention, and it can use a thing with various kinds of principal chain skeletons.

[0063]

Specifically A polyoxyethylene, polyoxypropylene, polyoxy butylene, Polyoxy tetramethylen, a polyoxyethylene polyoxypropylene copolymer, Polyoxyalkylene series polymers, such as a polyoxypropylene polyoxy butylene copolymer; An ethylene-propylene system copolymer, A copolymer of polyisobutylene, isobutylene, isoprene, etc., polychloroprene, A copolymer with polyisoprene, isoprene or butadiene, acrylonitrile, styrene, etc., A copolymer with polybutadiene, isoprene or butadiene, acrylonitrile, styrene, etc., Hydrocarbon system polymers, such as a hydrogenation polyolefine system polymer produced by hydrogenating these polyolefine system polymers; Condensation with dibasic acid, such as adipic acid, and glycol, Or a polyester system polymer obtained by ring opening polymerization of lactone; Ethyl (meta) acrylate, An acrylic ester system copolymer produced by carrying out the radical polymerization of the monomers, such as butyl (meta) acrylate (meta); (meta) An acrylic ester system monomer, vinyl acetate, acrylonitrile, A vinyl-base polymer produced by carrying out the radical polymerization of the monomers, such as styrene; A vinyl monomer in inside of said organic polymer is polymerized. Graft polymer; obtained. Polysulfide system polymer; Nylon 610 by condensation polymerization of nylon 6 by ring opening polymerization of epsilon caprolactam, hexamethylenediamine, Nylon 66 by condensation polymerization of adipic acid and hexamethylenediamine, and sebacic acid, Nylon 11 by condensation polymerization of epsilon-aminoundecanoic acid, A polycarbonate system polymer manufactured by carrying out condensation polymerization from polyamide system polymer, for example, bisphenol A, and carbonyl chlorides which have a two or more-ingredient ingredient among Nylon 12 by ring opening polymerization of epsilon-amino RAURO lactam, and the above-mentioned nylon, such as copolyamide, A diallyl phthalate system polymer etc. are illustrated. A polyoxyalkylene series polymer, a hydrocarbon system polymer, a polyester system polymer, an acrylic ester (meta) system copolymer, a polycarbonate system polymer, etc. are preferred from acquisition and manufacture being easy among polymers with the above-mentioned principal chain skeleton.

[0064]

Saturated hydrocarbon system polymers, such as polyisobutylene, hydrogenation polyisoprene, and hydrogenation polybutadiene, and a polyoxyalkylene series polymer and an acrylic ester (meta) system copolymer have a comparatively low glass transition temperature, and their hardened material obtained is preferred especially from excelling in cold resistance.

[0065]

In a principal chain skeleton of the above-mentioned organic polymer (A), other ingredients, such as a urethane bond ingredient, may be included in the range which does not spoil an effect of this invention greatly.

[0066]

It is not limited especially as the above-mentioned urethane bond ingradient, but For example, toluene (tolylene) diisocyanate, Aromatic system polyisocyanates, such as diphenylmethane

diisocyanate and xylylene diisocyanate; Isophorone diisocyanate, What is obtained from a reaction of polyisocyanate compounds, such as aliphatic series system polyisocyanates, such as hexamethylene di-isocyanate, and polyol which has various kinds of above-mentioned principal chain skeletons can be mentioned.

[0067]

If there are many amide segments (-NH-CO-) generated in a principal chain skeleton based on said urethane bond, viscosity of an organic polymer will become high and will serve as a bad constituent of workability. Therefore, as for quantity of an amide segment occupied in a principal chain skeleton of an organic polymer, it is preferred that it is 3 or less % of the weight, it is more preferred that it is 1 or less % of the weight, and it is most preferred that an amide segment is not included substantially.

[0068]

A reactive silicon group contained in an organic polymer which has a reactive silicon group is a basis which can construct a bridge by forming a siloxane bond by the reaction which has a hydroxyl group or a hydrolytic basis combined with a silicon atom, and is accelerated by a silanol condensation catalyst. As a reactive silicon group, it is a general formula (11). :

$-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (11)

an alkyl group of the carbon numbers 1-20 from which R^1 in a formula and R^2 were the same as or different. When the Tori ORGANO siloxy group shown by aryl group of the carbon numbers 6-20, an aralkyl group of the carbon numbers 7-20, or $(R')_3SiO-$ is shown and R^1 or two or more R^2 exist, they may be the same and may differ. R' is a hydrocarbon group of monovalence of the carbon numbers 1-20 here, and three R' may be the same and may differ. X shows a hydroxyl group or a hydrolytic basis, and when two or more X exists, they may be the same and may differ. As for a, 0, 1, 2, or 3b shows 0, 1, or 2, respectively. About b in m bases ($SiR^1_{2-b}X_bO$), they may be the same and may differ. m shows an integer of 0 to 19. however — what satisfies a+sigma b>=1 — carrying out — a basis expressed is raised.

[0069]

It is not limited but what is necessary is just a conventionally publicly known hydrolytic basis especially as a hydrolytic basis. Specifically, a hydrogen atom, a halogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an acid-amide group, an aminooxy group, a sulfhydryl group, an alkenyloxy group, etc. are mentioned, for example. Among these, a hydrogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an aminooxy group, a sulfhydryl group, and an alkenyloxy group are preferred, hydrolysis nature is quiet and a viewpoint of handling or a cone to especially an alkoxy group is preferred.

[0070]

A hydrolytic basis and a hydroxyl group can be combined with one silicon atom in the 1-3 ranges, and (a+sigmab) has 1-5 preferred ranges. When a hydrolytic basis and s hydroxyl group join togethar in [two or more] a reactive silicon group, they may be the same and may differ.

[0071]

In particular, it is a general formula (12). :

$-SiR^2_{3-a}X_a$ (12)

(R^2 and X are the same as the above among a formula.) Since a reactive silicon group expressed with an integer of 1-3 is easy to receive, a's is preferred.

[0072]

As an example of R^1 in the above-mentioned general formula (11) and (12), and R^2, For example, aralkyl groups, such as aryl groups, such as cycloalkyl groups, such as alkyl groups, such as a methyl group and an ethyl group, and a cyclohexyl group, and a phenyl group, and benzyl, the Tori ORGANO siloxy group R' is indicated to be by $(R')_3SiO-$ which is a methyl group, a phenyl group, etc. (R'), etc. are raised. Especially in these, a methyl group is preferred.

[0073]

As more concrete illustration of s reactive silicon group, a trimethoxysilyl group, a triethoxy silyl group, a trisopropoxy silyl group, a dimethoxymethyl silyl group, a diethoxymethylsilyl group, and a

diisopropoxy methyl silyl group are mentioned.
[0074]
Especially in this invention, an organic polymer which has the silicon containing functional group (that is, the number of a+bxm of a general formula (11) is three or more) which three or more hydrolytic bases combined on silicon in an organic polymer of the (A) ingredient can be used as an ingredient (A1).
[0075]
A hardened material which three or more hydrolytic bases had combined this (A1) ingredient on silicon, and constructed the bridge by a silanol condensation reaction of that reactive silicon group, Good stability is shown and remarkable creep resistance and an endurance improvement effect are shown as compared with a case of reactive silicon group containing organic polymer which has two or less hydrolytic bases.
[0076]
(A1) As for the number of a+bxm of a general formula (11) of an ingredient, it is more preferred that it is 3-5, and especially 3 is preferred. Also in it, since [that its improvement effect of the stability of a hardenability constituent of this invention, endurance, and creep resistance is especially large and] the Tori alkoxy silyl groups has the good availability of a raw material, it is preferred. Thing of an alkoxyl group of the carbon numbers 1-20 is preferred, its thing of the carbon numbers 1-10 is more preferred, and its thing of the carbon numbers 1-4 is still more preferred here. Specifically, a trimethoxysilyl group and a triethoxy silyl group are the most preferred. Hardenability may become late when a carbon number is larger than 20.
[0077]
Generally, if weight % of reactive silicon group containing organic polymer in a hardenability constituent becomes low, it is known that the endurance of a hardened material obtained will fall to **. However, if an ingredient (A1) of this invention is used as reactive silicon group containing organic polymer, high endurance is maintainable even if it makes low weight % of reactive silicon group containing organic polymer in a hardenability constituent. Therefore, five to 26% of the weight, when it is 15 to 24 % of the weight especially preferably, since a rate of an ingredient (A1) in a hardenability constituent is compatible in low cost and high endurance, it is more preferably preferred [rate] ten to 26% of the weight.
[0078]
Especially in this invention, an organic polymer which has the Tori alkoxy silyl groups of the carbon numbers 2-20 can be used as a (A4) ingredient in an organic polymer of an ingredient (A1). Namely, general formula (6) :

$-Si(OR^4)_3$ (6)

(three R^4 is the organic groups of monovalence of the carbon numbers 2-20 independently among a formula, respectively.) — an organic polymer which has a basis expressed can be used as a (A4) ingredient.
[0079]
It is known that methanol generated in connection with a hydrolysis reaction of a methoxy silyl group has peculiar toxicity of causing an obstacle of an optic nerve. On the other hand, since a carbon number of an alkoxy group which combines the (A4) ingredient with a silicon atom is 2 to 20, toxic high methanol is not contained in alcohol generated in connection with a hydrolysis reaction of a reactive silicon group, but serves as a constituent with high safety at it.
[0080]
(A4) It is preferred that it is especially 2-4, and when it is 2, it serves as ethanol, and since alcohol generated by hydrolysis has the highest safety, it is the most preferred [as for a carbon number of R^4 of a general formula (6) of an ingredient, it is more preferred that it is 2-10. and / alcohol]. Specifically, a triethoxy silyl group is the most preferred. When a carbon number is larger than 20, while the hardenability of a hardenability constituent may become late, an anesthetic action and stimulation of alcohol to generate may be large.
[0081]
Especially in this invention, a principal chain skeleton can use as a (A5) ingredient what is polyoxyalkylene in an organic polymer of the (A4) ingredient. Namely, general formula (6) :

$-Si(OR^4)_3$ (6)

A polyoxyalkylene series polymer which has a basis expressed with (R^4 in a formula is the same as the above) can be used as a (A5) ingredient.
[0082]
1.1-5 reactive silicon groups of an organic polymer (A) exist preferably [that average per molecule and at least one piece exists], and more preferably. If the number of reactive silicon groups contained in one molecule of organic polymers (A) will be less than one piece, hardenability will become insufficient and will become difficult to reveal a good rubber elasticity action. A reactive silicon group may exist in an end of an organic polymer (A) chain, and may exist in an inside. Since effective network chain density of an organic polymer (A) ingredient contained in a hardened material formed eventually will increase if a reactive silicon group exists in an end of s chain, a rubber-like hardened material in which a low elastic modulus is shown becomes is easy to be obtained by high intensity and high elongation.
[0083]
Especially in this invention, an organic polymer the number of reactive silicon groups per molecule averages, and 1.7-5 pieces exist in an organic polymer of the (A) ingredient can be used as an ingredient (A2).
[0084]
A hardened material which the number of reactive silicon groups per molecule averaged this (A2) ingredient for it, and 1.7-5 pieces existed, and constructed the bridge by a silanol condensation reaction of that reactive silicon group, Good stability is shown, the number of reactive silicon groups per molecule averages, and remarkable creep resistance and an endurance improvement effect are shown as compared with a case of less than 1.7 organic polymers.
[0085]
(A2) As for the number of reactive silicon groups per molecule of an ingredient, it is more preferred that they are 2-4 pieces, and it is preferred that they are especially 2.3-3 pieces. When there are few 1.7 reactive silicon groups per molecule, an improvement effect of the stability of s hardenability constituent of this invention, endurance, and creep resistance may not be enough, and when larger than five pieces, elongation of s hardened material obtained may become small.
[0086]
Especially at this invention, it is a general formula in an organic polymer of the (A) ingredient (3). :

$-O-R^3-CH(CH_3)-CH_2-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (3)

(R^3 in a formula a divalent organic group of the carbon numbers 1-20 which contain one or more sorts chosen from a group which consists of hydrogen, oxygen, and nitrogen as a composition atom) [show and] R^1, R^2, X, a, b, and m — the above -- it is the same — an organic polymer which has a structure part with which it is expressed can be used as a (A3) ingredient.
[0087]
A hardened material which this (A3) ingredient has a structure part expressed with a general formula (3), and constructed the bridge by a silanol condensation reaction of that reactive silicon group shows good stability, and shows remarkable creep resistance and an endurance improvement effect as compared with a case of an organic polymer which has terminal structures other than a general formula (3).
[0088]
As for s carbon number of R^3 of a general formula (3), it is more preferred from s point of availability that it is 1-10, and it is preferred that it is especially 1-4. Specifically, R^3 has the most preferred methylene group.
[0089]
(A3) An ingredient is a general formula (5). :

$-O-R^3-CH(CH_3)-CH_2-SiX_3$ (5)

(R^3 in a formula and X are the same as the above.) — when it is an organic polymer which has a structure part with which it is expressed, since [that an improvement effect of the stability of a hardenability constituent of this invention, endurance, and creep resistance is especially large and]

the availability of a raw material is good, it is desirable.
[0090]
(A) What is necessary is just to perform introduction of a reactive silicon group of an ingredient by a publicly known method. That is, the following methods are mentioned, for example.
[0091]
(b) Make an organic compound which has an active group and an unsaturation group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, in a molecule to this functional group react, and obtain an organic polymer containing an unsaturation group. Or an unsaturation group content organicity polymer is obtained by copolymerization with an unsaturation group content epoxy compound. Subsequently, hydrosilane which has a reactive silicon group is made to act on an acquired resultant, and it hydrosilylates.
[0092]
(**) Make a compound which has a sulfhydryl group and a reactive silicon group react to an organic polymer containing an unsaturation group produced by making it be the same as that of the (b) method.
[0093]
(**) Make a compound which has a functional group and a reactive silicon group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, an epoxy group, and an isocyanate group, in a molecule to this functional group react.
[0094]
Since a high inversion rate is obtained in comparatively short reaction time, a method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group react to an and a method of (b) or among (**)s in the above method is preferred. An organic polymer which has the reactive silicon group obtained by a method of (b), (**) Since becoming a good hardenability constituent of workability by hypoviscosity rather than an organic polymer obtained by a method and an organic polymer obtained by a method of (**) have the strong bad smell based on an mercaptosilane, especially its method of (b) is preferred.
[0095]
(b) As an example of a hydrosilane compound used in a method. For example, trichlorosilane, methyldi chlorosilicane, dimethylchlorosilicane, Halogenation Silang like phenyl dichlorosilane; Trimethoxysilane, Triethoxysilane, methyldiethoxysilane, methyl dimethoxysilane, The alkoxysilane like phenyl dimethoxysilane; Methyldi acetoxysilane, The acyloxy silanes like a phenyldiacetoxysilane; although the KETOKISHI mate silanes like bis(dimethyl KETOKISHI mate)methylsilane and bis(cyclohexyl KETOKISHI mate)methylsilane are raised, it is not limited to these. Especially among these, halogenation Silang and alkoxysilana are preferred, especially alkoxysilane has the quiet hydrolysia nature of a hardenability constituent obtained, and it is the most preferred to a handling and cone sake.
[0096]
In the above-mentioned hydrosilana compound, it is a general formula (2). :

$$H\text{-}SiX_3 \quad (2)$$

Since a hydrosilane compound expressed with (X in a formula is the same as the above) has an especially large improvement effect of the stability of a hardenability constituent which consists of an organic polymer obtained by an addition reaction of this hydrosilane compound, endurance, and creep resistance, it is preferred. In a hydrosilane compound expressed with a general formula (2), trialkoxysilane, such as trimethoxysilane, triethoxysilane, and a triisopropoxy silane, is more preferred.

[0097]
trialkoxysilane in which carbon numbers, such as trimethoxysilane, have an alkoxy group (methoxy group) of 1 also in said trialkoxysilane is like [when disproportionation may advance quickly and disproportionation progresses] dimethoxysilane — a dangerous compound arises in inside. From a viewpoint of safety on handling to a general formula (9) :

$$H\text{-}Si(OR^4)_3 \quad (9)$$

It is preferred to use trialkoxysilana which has an alkoxy group whose carbon number expressed with (R^4 in a formula is the same as the above) is two or more. A viewpoint of availability, safety [on

handling], stability [of a hardenability constituent obtained], endurance, and creep resistance ** to triethoxysilane is the most preferred.
[0098]
(**) Although a method of introducing into an unsaturation binding site of an organic polymer a compound which has a sulfhydryl group and a reactive silicon group as a synthetic method by a radical addition reaction under a radical initiator and/or radical source-of-release existence, for example, etc. are mentioned, it is not limited in particular. As an example of a compound of having said sulfhydryl group and a reactive silicon group, For example, although gamma-mercapto propyltrimethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, gamma-mercaptopropyl triethoxysilane, gamma-mercapto propylmethyl diethoxysilane, etc. are raised, it is not limited to these.
[0099]
(**) Although a method etc. which are shown in JP,H3-47825,A are mentioned, for example as a method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group reacting to an and among synthetic methods, it is not limited in particular. As an example of a compound of having said isocyanate group and a reactive silicon group, For example, although gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propylmethyl dimethoxysilane, gamma-isocynatepropyl triethoxysilane, gamma-isocyanate propylmethyl diethoxysilane, etc. are raised, it is not limited to these.
[0100]
As mentioned above, as for a silane compound which three hydrolytic bases have combined with one silicon atoms, such as trimethoxysilane, disproportionation may advance. As for trialkoxysilane in which especially carbon numbers, such as trimethoxysilane, have an alkoxy group (methoxy group) of 1, disproportionation may advance quickly. If disproportionation progresses, a remarkable dangerous compound [like] which is dimethoxysilane will arise. However, such disproportionation advances in neither gamma-mercapto propyltrimethoxysilane nor gamma-isocyanate propyltrimethoxysilane. For this reason, when using the Tori alkoxy silyl groups which has methoxy groups, such as a trimethoxysilyl group, as a silicon content group, it is preferred to use a synthetic method of (**) or (**).
[0101]
As how to obtain an organic polymer which has the silicon content group combined with a methoxy group, it is one method of the above-mentioned (**), (**), and (**), and a reactive silicon group is a general formula (6). :

$$-Si(OR^4)_3 \quad (6)$$

A compound (J) which has at least one methoxy group which can carry out an ester exchange reaction after obtaining an organic polymer (getting it blocked the above-mentioned (A4) ingredient) which has a basis expressed with (R^4 in a formula is the same as the above), It is a general formula by carrying out an aster exchange reaction under existence of a transesterification catalyst or nonexistence (10). :

$$-Si(OCH_3)_f(OR^4)_{3-f} \quad (10)$$

(among a formula, 3-f R^4 is the organic groups of monovalence of the carbon numbers 2-20 independently, respectively, and f shows 1, 2, or 3.) — a method of manufacturing an organic polymer which has a basis expressed can be mentioned. An organic polymer which has a basis expressed with a general formula (10) shows fast curability rather than an organic polymer which has a basis expressed with a general formula (6).
[0102]
In said manufacturing method, after introducing a reactive silicon group especially by a method of (**), by carrying out an ester exchange reaction to the aforementioned (J) ingredient, A method of manufacturing an organic polymer which has a basis expressed with a general formula (10), Without a dangerous compound like dimethoxysilane by disproportionation arising in the middle of manufacture, there are few bad smells, and also since it becomes a good hardenability constituent of workability by hypoviacosity rather than an organic polymer obtained by a method of (**), it is more desirable than an organic polymer obtained by a method of (**).
[0103]

As a compound (J) which has at least one above-mentioned methoxy group which can carry out an ester exchange reaction, there is no limitation in particular and various kinds of compounds can be used.

[0104]

A compound etc. which have the silicon atom combined with methyl ester of various kinds of acid, such as methanol, carboxylic acid, and sulfonic acid, and at least one methoxy group as a (J) ingredient here can be mentioned. Since a compound which has the silicon atom united with 2-4 methoxy groups on the same silicon atom as a compound which has the silicon atom combined with said at least one methoxy group has a quick ester exchange reaction speed, it is preferred. Since especially a compound that has a silicon atom united with 2-4 methoxy groups on the same silicon atom and an amino group has a quick ester exchange reaction speed, it is preferred.

[0105]

When it illustrates concretely, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, Amino group content Silang, such as gamma-ureido propyltrimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, and N-benzyl-gamma-aminopropyl trimethoxysilane, can be mentioned. A denatured derivative and a condensation reaction thing of the above-mentioned silane compound can also use the above-mentioned silane compound as a (J) ingredient.

[0106]

Since an ester exchange reaction advances also under existence of a transesterification catalyst and comparatively low temperature conditions 60 ** or less, aforementioned amino group content Silang is preferred.

[0107]

As for the (J) ingredient used for this invention, it is preferred to use and carry out an ester exchange reaction in 0.1-10 copies to 100 copies of reactive silicon group containing organic polymer of the (A4) ingredient. It is preferred to use it in 1-5 copies especially. The above-mentioned (J) ingredient may be used only by one kind, and may carry out two or more kind mixing use.

[0108]

An organic polymer (A) which has a reactive silicon group may have straight chain shape or branching, and the number average molecular weight is 1,000-30,000 more preferably 500 to about 50,000 in polystyrene conversion in GPC. When there is a tendency whose number average molecular weight is inconvenient in respect of the extension characteristic of a hardened material at less than 500 and 50000 is exceeded, since it becomes hypervicosity, there is an inconvenient tendency in respect of workability.

[0109]

A reactive silicon group may be in an end or an inside of an organic polymer chain, and may be in both. Since effective network chain density of an organic polymer component contained in a hardened material formed eventually increases especially when a reactive silicon group is in a molecular terminal, it is desirable from points, like a rubber-like hardened material of high elongation becomes is easy to be obtained with high intensity.

[0110]

Said polyoxyalkylene series polymer is a general formula intrinsically (13). :

[0111]

[Formula 1]

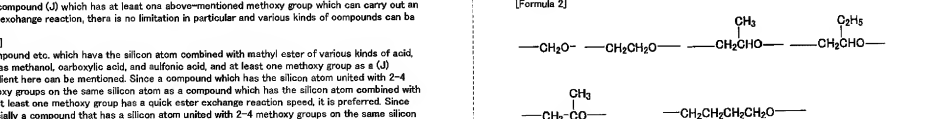
$$—R^9—O— \quad (13)$$

[0112]

(among a formula, R^9 is a divalent organic group and is the straight chain shape or the branching alkylene group of the carbon numbers 1-14.) — it being a polymer which has a repeating unit shown, and, R^9 in a general formula (13) has the carbon numbers 1-14, and also preferred straight chain shape or branched state alkylene group of 2-4. As the example of the repeating unit shown by a general formula (13),

[0113]

[Formula 2]



[0114]

** is mentioned. The principal chain skeleton of a polyoxyalkylene series polymer may consist of one kind of repeating unit, and may consist of two or more kinds of repeating units. When used especially for sealant etc., it is desirable from that what comprises the polymer which uses a propylene oxide polymer as the main ingredients is amorphous, or the point which is hypoviscosity comparatively.

[0115]

As a synthetic method of a polyoxyalkylene series polymer, For example, the polymerizing method by an alkali catalyst like KOH, the polymerizing method by a transition metal compound-porphyrin complex catalyst like a complex produced by making an organoaluminium compound and porphyrin which are shown in JP,61-215623,A react, JP,46-27250,B, JP,59-15336,B, a U.S. Pat. No. 3278457 item, a U.S. Pat. No. 3278458 item, A U.S. Pat. No. 3278459 item, a U.S. Pat. No. 3427256 item, a U.S. Pat. No. 3427334 item, The polymerizing method by a composite metal cyanide complex catalyst shown in a U.S. Pat. No. 3427335 item etc., **********, such as the polymerizing method using a catalyst which consists of a polyphosphazene salt illustrated by JP,H10-273512,A, and the polymerizing method using a catalyst which consists of a phosphazene compound illustrated by JP,H11-060722,A, are not limited in particular.

[0116]

A manufacturing method of a polyoxyalkylene series polymer which has a reactive silicon group, JP,45-36319,B, 46-12154, JP,50-156599,A, 54-6096, 55-13767, 55-13468, What is proposed by each gazette, such as 57-164123, JP,3-2450,B, U.S. Pat. No. 3632557, U.S. Pat. No. 4345053, U.S. Pat. No. 4366307, and U.S. Pat. No. 4960844, JP,61-197631,A, 61-215522, 61-215523, Although 8,000 or more number average molecular weights and Mw/Mn which are proposed by each gazette of 61-218632, JP,H3-72527,A, JP,H3-47825,A, and JP,H8-231707,A can illustrate a polyoxyalkylene series polymer with narrow molecular weight distribution in the 1.6 or less amount of Polymer Division, It is not limited to in particular these.

[0117]

A polyoxyalkylene series polymer which has the above-mentioned reactive silicon group may be used alone, and may be used together two or more sorts.

[0118]

Said saturated hydrocarbon system polymer is a polymer which does not contain substantially carbon-carbon unsaturated bonds other than an aromatic ring, and a polymer which makes the skeleton, (1). [whether an olefinic compound of the carbon numbers 1-6, such as ethylene, propylene, 1-butene, and isobutylene, is polymerized as a main monomer, and] (2) After making diene series, such as butadiene and isoprene, homopolymerize or carrying out copolymerization of the above-mentioned olefinic compound, can obtain by a method of hydrogenating, but. Since an isobutylene system polymer and a hydrogenation polybutadiene system polymer tend to introduce a functional group into an end, and tend to control a molecular weight and can increase the number of end functional groups, they are preferred, and a composite ease to especially their isobutylene system polymer is prefarred.

[0119]

That whose principal chain skeleton is a saturated hydrocarbon system polymer has the feature

which is excellent in heat resistance, weatherability, endurance, and humidity interception nature.
[0120]
All the monomeric units may be formed from an isobutylene unit, and an isobutylene system polymer, Although a copolymer with other monomers may be sufficient, what contains a repeating unit which originates in isobutylene from a field of rubber property 50% of the weight or more is preferred, what is contained 80% of the weight or more is more preferred, and especially a thing contained 90 to 99% of the weight is preferred.
[0121]
As a synthetic method of a saturated hydrocarbon system polymer, although various polymerization methods are reported conventionally, especially living polymerization what is called of recent years many is developed. an iniphor polymerization (J. — P.Kennedy et al.) which was found out by Kennedy and others in the case of a saturated hydrocarbon system polymer, especially an isobutylene system polymer J. Polymer Sci. and Polymer Chem. Ed. 1997. By using 15 volumes and 2843 pages, manufacturing casily is possible, about 500 to 100,000 molecular weight can be polymerized in 1.5 or less molecular weight distribution, and it is known that various functional groups can be introduced into a molecular terminal.
[0122]
As a process of a saturated hydrocarbon system polymer which has a reactive silicon group, For example, JP,4-69659,B, JP,7-108928,B, JP,63-254149,A, Although it writes in each Description of JP,64-22904,A, JP,1-197509,A, Patent Gazette No. 2539445, Patent Gazette No. 2873395, and JP,7-53882,A, it is not limited to in particular these.
[0123]
It is a general formula in a saturated hydrocarbon system polymer which has the above-mentioned reactive silicon group (6). :

$$-Si(OR^4)_3 \quad (6)$$

Especially (A7) a saturated hydrocarbon system polymer that has a basis expressed with (R^4 in a formula is the same as the above) can be used as an ingredient. This (A7) ingredient has the feature which is excellent in heat resistance based on a saturated hydrocarbon system polymer, weatherability, and humidity interception nature of a principal chain skeleton, and does not have generation of methanol accompanying a hydrolysis reaction of a reactive silicon group, and is a polymer whose stability of a hardened material, endurance, and creep resistance are still better.
[0124]
A saturated hydrocarbon system polymer which has the above-mentioned reactive silicon group may be used alone, and may be used togather two or more sorts.
[0125]
Especially in this invention, a chain can use what is an acrylic estar (meta) system copolymer as an ingredient (A6) in an organic polymer of the (A) ingredient.
[0126]
Especially as an acrylic ester (meta) system monomer which constitutes a main chain of the aforementioned (meta) acrylic ester system polymer, it is not limited but various kinds of things can be used. If it illustrates, acrylic acid (meta), methyl acrylate (meta), (Meta) Ethyl acrylate, acrylic acid (meta)-n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-n-pentyl, (Meta) Acrylic acid-n-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-n-heptyl, acrylic acid (meta)-n-octyl, (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) Acrylic acid tolyl, acrylic acid (meta) benzyl, acrylic acid (meta)-2-methoxy ethyl, (Meta) Acrylic acid-3-methoxy butyl, acrylic acid (meta)-2-hydroxyethyl, (Meta) Acrylic acid-2-hydroxypropyl, acrylic acid (meta) stearyl, metaglycidyl acrylate (meta), acrylic acid (meta) 2-aminoethyl, gamma-(methacryloyl oxypropyl) trimethoxysilane, an ethylenoxoide addition of acrylic acid (meta), (Meta) Acrylic acid trifluoromethyl methyl, an acrylic acid (meta) 2-trifluoro methylethyl, (Meta) Acrylic acid 2-perfluoro ethylethyl, acrylic acid (meta) 2-perfluoro ethyl-2-perfluoro butylethyl, (Meta) Acrylic acid 2-perfluoro ethyl, acrylic acid (meta) perfluoro methyl, (Meta) Acrylic acid JIPA fluoromethylmethyl, acrylic acid (meta) 2-perfluoro methyl-2-perfluoro athylmethyl, (Meta) Acrylic acid series (meta) monomers, such as acrylic acid 2-perfluoro hexylethyl, acrylic acid (meta) 2-perfluoro decylethyl, and acrylic acid (meta) 2-perfluoro hexadecylethyl, etc. are mentioned. In the

aforementioned (meta) acrylic ester system copolymer, copolymerization of the following vinyl system monomers can also be carried out with an acrylic ester (meta) system monomer. When this vinyl system monomer is illustrated, styrene, vinyltoluene, alpha-methylstyrene, Styrene system monomers, such as KURORU styrene, styrene sulfonic acid, and its salt; Perfluoro ethylene, Fluoride ocntent vinyl monomers, such as perfluoro propylens and vinylidene fluoride; Vinyltrimetoxysilane, Silicon content vinyl system monomers, such as vinyltriethoxysilans; A maleic anhydride, Monoalkyl ester and dialkyl ester of maleic acid and maleic acid; Fumaric acid, Monoalkyl ester and dialkyl ester of fumaric acid; Maleimide, Methylmaleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexylmaleimide, octylmaleimide, dodecylmaleimide, stearyl maleimide, Maleimide system monomers, such as phenylmaleimide and cyclohexylmaleimide; Acrylonitrile, Nitrile group content vinyl system monomers, such as a methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Alkenes; butadiene, such as vinyl ester; ethylene, such as vinyl acetate, vinyl propionate, vinyl pivalate, benzoic acid vinyl, and vinyl cinnamic acid, and propylene, Conjugated dienes, such as isoprene; VCM/PVC, a vinylidene chloride, an allyl chloride, allyl alcohol, etc. are mentioned. These may be used independently, and even if it carries out copolymerization of the plurality, they are not cared about. Especially, a polymer which consists of a styrene system monomer from physical properties etc, and (meta) an acrylic acid series monomer of output is preferred. It is an acrylic polymer which consists of acrylic ester monomer and a methacrylic-acid-ester monomer (meta) more preferably, is an acrylic polymer which consists of acrylic aster monomer preferably especially, and is a polymer which consists of butyl acrylatee still more preferably. A point that physical properties. such as hypovicosity of a compound, a low modulus of a hardened material, high elongation, weatherability, and heat resistance, are required in a use of general ******** to a butyl acrylate system monomer is still more preferred. A copolymer mainly concerned with ethyl acrylats on the other hand in a use as which oil resistance, such as an automotive application, etc. are required is still more preferred. It can also transpose a part of ethyl acrylate to butyl acrylate in order to raise that low-temperature characteristic, since it tends to be a little inferior to the low-temperature characteristic (cold resistance), although a polymer mainly concerned with this ethyl acrylate is excellent in oil resistance. However, since it follows on increasing a ratio of butyl acrylate and the good oil resistance is spoiled, as for the ratio, for a use of which oil resistance is required, it is preferred to carry out to 40% or less. and also it is more preferred to make it to 30% or less. In order to improve the low-temperature characteristic etc., without spoiling oil resistance, it is also preferred to use acrylic acid 2-methoxy ethyl, acrylic acid 2-ethoxyethyl, etc. by which oxygen was introduced into an alkyl group of a side chain. However, since it is in a tendency for heat resistance to be inferior by introduction of an alkoxy group which has an ether bond in a side chain, when heat resistance is required, it is preferred [the ratio] to make it to 40% or less. It is possible to obtain a polymer which changed the ratio and was suitable in consideration of physical properties needed, such as oil resistance, heat resistance, and the low-temperature characteristic, according to a various application or the purpose demanded. For example, as an example which is excellent in properties balance, such as oil resistance, heat resistance, the low-temperature characteristic, although limitation is not carried out, a copolymer of ethyl acrylata / butyl acrylate / acrylic acid 2-methoxy ethyl (it is 40-50/20-30/30-20 at a weight ratio) is mentioned. In this invention, it is preferred other monomers, copolymerization, and also that may carry out block copolymerization and these desirable monomers are contained not less than 40% by a weight ratio in these desirable monomers in that case. Acrylic acid (meta) expresses acrylic acid and/, or methacrylic acid with the above-mentioned expressive form.
[0127]
(Meta) It is not limited but what is necessary is just to carry out by a publicly known method especially as a synthetic method of an acrylic ester system copolymer (A6). However, it has the problem that a polymer obtained by the usual free radical polymerizing method using an azo compound, a peroxide, etc. as a polymerization initiator generally has a value of molecular weight distribution as large as two or more, and viscosity becomes high. Therefore, molecular weight distribution is narrow, and in order to obtain an acrylic sater system copolymer which has a cross-linking functional group in molecular chain terminals at a high rate (meta), it is preferred [it is an acrylic ester system copolymer with low (meta) viscosity, and] to use a living-radical-polymerization method.

[0128]
Also in a "living-radical-polymerization method", an organic halogenated compound or a sulfonyl halide compound An initiator, An "atom-transfer-radical-polymerization method" which polymerizes an acrylic ester (meta) system monomer by making a transition metal complex into a catalyst, As a manufacturing method of an acrylic ester system copolymer which in addition to the feature of the above-mentioned "living-radical-polymerization method" has halogen comparatively advantageous to a functional group conversion reaction etc. at the end, and has a specific functional group from flexibility of a design of an initiator or a catalyst being large (meta), it is still more desirable. 117 volumes, 5614 pages, etc. will be mentioned as this atom-transfer-radical-polymerization method in Matyjaszewski et al. and journal OBU American chemical society (J. Am.Chem.Soc.) 1995.
[0129]
A hardened material produced by hardening a hardenability constituent containing an acrylic ester system copolymer which has a reactive silicon group (meta) may have low elongation as compared with a hardenability constituent containing an organic polymer which has other principal chain skeletons, such as a polyoxyalkylene series polymer. Even if it uses an acrylic ester (meta) system copolymer manufactured using the above "living-radical-polymerization method" and an "atom-transfer-radical-polymerization method", elongation may be insufficient and endurance may be bad. As compared with an organic polymer which can improve notably the endurance of this (meta) acrylic ester system copolymer by using an silicon a silicon containing functional group which has three or more hydrolytic bases as a reactive silicon group, and has other principal chain skeletons, an endurance improvement effect is large.
[0130]
As a process of an acrylic ester system copolymer which has a reactive silicon group (meta), a process using the free radical polymerizing method for having used a chain transfer agent for JP,H3-14068,B, JP,H4-55444,B, JP,H6-211922,A, etc. is indicated, for example. Although a process which used an atom-transfer-radical-polymerization method for JP,H9-272714,A etc. is indicated, it is not limited to in particular these.
[0131]
It is a general formula in an acrylic ester system copolymer which has the above-mentioned reactive silicon group (meta) (6). :

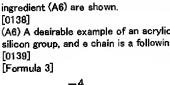
$-Si(OR^4)_3$ (6)

especially (A8) an acrylic ester system copolymer that has a basis expressed with (R^4 in a formula is the same as the above) (meta-) can be used as an ingredient. Heat resistance based on an acrylic ester (meta) system copolymer of a principal chain skeleton in this (A8) ingredient, It has the feature which is excellent in weatherability and chemical resistance, and there is no generation of methanol accompanying a hydrolysis reaction of a reactive silicon group, and it is a polymer whose stability of a hardened material, endurance, and creep resistance are still better.
[0132]
A reactive silicon group of the aforementioned (A8) ingredient may be in an end or an inside of an organic polymer chain, and may be in both. Since effective network chain density of a polymer component contained in a hardened material formed eventually increases especially when a reactive silicon group is in an end of a polymer main chain, it is desirable from points, like a rubber-like hardened material of high elongation becomes is easy to be obtained with high intensity.
[0133]
As a polymerization method of the aforementioned (A8) ingredient, when a living-radical-polymerization method is used, since molecular weight distribution is narrow, it is hypoviscosity, and from the ability to introduce a cross-linking functional group into molecular chain terminals at a high rate, it is more desirable and especially an atom-transfer-radical-polymerization method is preferred.
[0134]
An acrylic ester system copolymer which has the above-mentioned reactive silicon group (meta) may be used alone, and may be used together two or more sorts.
[0135]
An organic polymer which has these reactive silicon groups may be used alone, and may be used together two or more sorts. Specifically, a polyoxyalkylene series polymer which has a reactive silicon group, a saturated hydrocarbon system polymer which has a reactive silicon group, an acrylic ester

system copolymer which has a reactive silicon group (meta), and an organic polymer which blends two or more sorts chosen from a group, ** and others, can also be used.
[0136]
A manufacturing method of an organic polymer which blends a polyoxyalkylene series polymer which has a reactive silicon group, and an acrylic ester system copolymer which has a reactive silicon group (meta), Although proposed by JP,59-122541,A, JP,63-112642,A, JP,H6-172631,A, JP,H11-116763,A, etc., it is not limited to in particular these.
[0137]
It is known as compared with a case where a polyoxyalkylene series polymer is independently used for an organic polymer which blends a polyoxyalkylene series polymer which has this reactive silicon group, and an acrylic ester system copolymer which has a reactive silicon group (meta) that stability is bad. Then, the above-mentioned general formula (6) as a polyoxyalkylene series polymer component in the aforementioned organic polymer to blend :

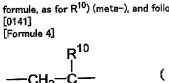
$-Si(OR^4)_3$ (6)

A polyoxyalkylene series polymer (A5) which has a basis expressed with (R^4 in a formula is the same as the above) is used, An organic polymer blended with an acrylic ester system copolymer (A6) which has a reactive silicon group (meta) has outstanding stability, endurance, and creep resistance based on the (A5) ingredient, while outstanding weatherability and an adhesive property based on an ingredient (A6) are shown.
[0138]
(A6) A desirable example of an acrylic ester (meta) system copolymer of an ingredient has a reactive silicon group, and a chain is a following general formula substantially (14). :
[0139]
[Formula 3]



(14)

[0140]
the acrylic ester monomer unit which has an alkyl group of the carbon numbers 1-8 expressed with (a hydrogen atom or a methyl group, and R^{11} show the alkyl group of the carbon numbers 1-8 among a formula, as for R^{10}) (meta-), and following general formula (15):
[0141]
[Formula 4]



(15)

[0142]
(— the inside of a formula, and R^{10} — the above — the same — R^{12} shows a with a carbon numbers of ten or more alkyl group —) — to a copolymer which consists of an acrylic ester monomer unit which has a with a carbon numbers of ten or more expressed alkyl group (meta-). It is the method of blending and manufacturing a polyoxyalkylene series polymer which has a reactive silicon group.
[0143]
as R^{11} of said general formula (14) — the carbon numbers 1-8 of a methyl group, an ethyl group, a

propyl group, n-butyl group, t-butyl group, a 2-ethylhexyl group, etc. — desirable — 1-4 — an alkyl group of 1-2 is raised still more preferably. An alkyl group of R^{11} may be independent and may be mixed two or more sorts.

[0144]

as R^{12} of said general formula (15) — ten or more carbon numbers of a lauryl group, a tridecyl group, a cetyl group, a stearyl group, a behenyl group, etc. — usually — 10-30 — a long-chain alkyl group of 10-20 is raised preferably. Like a case of R^{11}, an alkyl group of R^{12} may be independent and may be mixed two or more sorts.

[0145]

Although a chain of a ** (meta) acrylic ester system copolymer consists of a monomeric unit of a formula (14) and a formula (15) substantially, a "real target" here means that the sum total of a monomeric unit of a formula (14) which exists in this copolymer, and a formula (15) surpasses 50 % of the weight. The sum total of a monomeric unit of a formula (14) and a formula (15) is 70 % of the weight or more preferably.

[0146]

As for an abundance ratio of a monomeric unit of a formula (14), and a monomeric unit of a formula (15), 95:5-40:60 are preferred at a weight ratio, and 90:10-60:40 are still more preferred.

[0147]

As monomeric units other than a formula (14) which may be contained in this copolymer, and a formula (15), For example, acrylic acid, such as acrylic acid and methacrylic acid; Acrylamide, Amide groups, such as methacrylamide, N-methylolacrylamide, and N-methylolmethacrylamide, Epoxy groups, such as glycidyl acrylate and glycidyl methacrylate, Diethylamino ethyl acrylate, diethylamino ethyl methacrylate, A monomer containing amino groups, such as aminoethyl vinyl ether; a monomeric unit which originates in acrylonitrile, styrene, alpha-methylstyrene, alkyl vinyl ether, VCM/PVC, vinyl acetate, vinyl propionate, ethylene, etc. in addition to this is raised.

[0148]

Although an organic polymer which blends a saturated hydrocarbon system system polymer which has a reactive silicon group, and an acrylic ester system copolymer which has a reactive silicon group (meta) is proposed by JP,H1-168764,A, JP,2000-186176,A, etc., It is not limited to in particular these.

[0149]

A method of polymerizing an acrylic ester (meta) system monomer elsewhere under existence of an organic polymer which has a reactive silicon group as a manufacturing method of an organic polymer which blends an acrylic ester system copolymer which has a reactant silicon functional group (meta) can be used. Although this manufacturing method is concretely indicated by each gazette, such as JP,59-78223,A, JP,59-168014,A, JP,60-228516,A, and JP,60-228517,A, it is not limited to these.

[0150]

In this invention, silicate can be used as a (B) ingredient. This silicate has the function to improve the stability of an organic polymer which is the (A) ingredient of this invention, endurance, and creep resistance.

[0151]

(B) Silicate which is an ingredient is a general formula (16).

$SiOR^{13}{}_4$ (16)

the inside of a formula, and R^{13} — respectively — independent — a hydrogen atom or an alkyl group of the carbon numbers 1-20. They are an aryl group of the carbon numbers 6-20, and the univalent hydrocarbon group chosen from an aralkyl group of the carbon numbers 7-20. They are tetra alkoxysilane expressed or its partial hydrolysis condensate.

[0152]

As an example of silicate, for example A tetramethoxy silane, a tetraethoxysilane, Ethoxy trimethoxysilane, dimethoxy diethoxysilane, methoxy triethoxysilane, Tetra alkoxysilane (tetraalkyl silicate), such as tetra n-propoxysilane, tetra i-propoxysilane, tetra n-butoxysilane, tetra i-butoxysilane, and tetra t-butoxysilane, and those partial hydrolysis condensates are raised.

[0153]

Since a partial hydrolysis condensate of tetra alkoxysilane has an improvement effect of the stability

of this invention, endurance, and creep resistance larger than tetra alkoxysilane, it is preferred.

[0154]

A thing which was made to add and carry out partial hydrolyzate of the water to tetra alkoxysilane by a usuel method as a partial hydrolysis condensate of said tetra alkoxysilane for example, and was made to condense is raised. A commercial thing can be used for a partial hydrolysis condensate of an ORGANO silicate compound. As such a condensate, the methylsilicate 51, the ethyl silicate 40 (all are made in Col Coat), etc. are mentioned, for example.

[0155]

Silicate (B) shows an improvement effect of still better stability, endurance, and creep resistance by combining with an ingredient (A1) of this invention, an ingredient (A2), and the (A3) ingredient. By combining with an ingredient (A1) especially shows an improvement effect of good stability, endurance, and creep resistance.

[0156]

(B) As amount of ingredient used, 0.1 - 10 weight section is preferred to (A) ingredient 100 weight section, and also 1 - 5 weight section is preferred. (B) If loadings of an ingredient are less than this range, an improvement effect of stability, endurance, and creep resistance may not be enough, and a cure rate may become slow if loadings of the (B) ingredient exceed this range. The above-mentioned silicate may be used only by one kind, and may carry out two or more kind mixing use.

[0157]

In this invention, carboxylic acid tin salt can be used as a (C) ingredient. As compared with other silanol condensation catalysts, the stability of a hardened material obtained, endurance, and creep resistance can be improved by using this carboxylic acid tin salt as a silanol condensation catalyst of an organic polymer which is an ingredient (A1) of this invention.

[0158]

Limitation in particular does not have carboxylic acid tin salt (C) used for this invention, and various kinds of compounds can be used for it.

[0159]

As carboxylic acid which has an acid radical of carboxylic acid tin salt (C) here, a carboxylic acid group content compound of a hydrocarbon system of 2-40 is suitably used for a carbon number including carbonyl carbons, and carboxylic acid of a hydrocarbon system of the carbon numbers 2-20 may be especially used suitably from a point of availability.

[0160]

When it illustrates concretely, acetic acid, propionic acid, butanoic acid, a valeric acid, caproic acid, Enanthic acid, caprylic acid, 2-ethylhexanoic acid, pelargonic acid, capric acid, Undecanoic acid, lauric acid, tridecylacid, myristic acid, pentadecyl acid, Palmitic acid, heptadecylacid, stearic acid, nonadecanoic acid, arachin acid, Behenic acid, lignoceric acid, cerinic acid, montanic acid, melissic acid, Straight chain saturated fatty acid groups, such as RAKUSERU acid; Undecylenic acid, Linder acid, Tsuzuic acid, FIZETERIN acid, myristoleic acid, 2-hexadecenoic acid, 6-hexadecenoic acid, 7-hexadecenoic acid, palmitolcic acid, e petroselinic acid, Oleic acid, elaidic acid, ASUKUREPIN acid, veccenic acid, gadoleic acid, Gondo Inn acid, a catoleic acid, erucic acid, brassidic acid, eelacholeic acid, KISHIMEN acid, RUMEKUEN acid, acrylic acid, methacrylic acid, angelic acid, Monoene unsaturated fatty acid, such as crotonic acid, isocrotonic acid, and 10-undecenoic acid; Rano elaidic acid, Linolic acid, 10,12-octadecadienoic acid, HIRAGO acid, alpha-eleostearic acid, beta-eleostearic acid, punicic acid, linolenic acid, 8,11,14-eicosatrienoic acid, A 7,10,13-docosatrienoic acid, 4,8,11,14-hexadeca tetraenoic acid, MOROKUCHI acid, steer RIDON acid, arachidonic acid, 8, 12 and 16, 19-docosatetraenoic acid, 4,8,12,15,18-eicosapentaenoic acid, clupanodonic acid, herring acid, Polyene unsaturated fatty acid, such as docosahexenoic acid; 1-methylbutyric acid, Isobutyric acid, 2-ethylbutanoic acid, isovaleric acid, tuberculostearic acid, Branch fatty acid, such as a pivalic acid and neo decanoic acid; PUROPI all acid, a tariric acid, Fatty acid with triple bonds, such as steer roll acid, a crepenynic acid, KISHIMENIN acid, and 7-hexa creper-de-Chine acid; Naphthenic acid, A malvalic acid, sterculic acid, HIDONO carbyne acid, chaulmoogric acid, Alicyclic carvone acids, such as gorlic acid; Acetoacetic acid, ethoxyacetic acid, Glyoxylic acid, glycolic acid, gluconic acid, sabinic acid, 2-hydroxytatradecanoic acid, IPURORU acid, 2-hydroxyhexedecenoic acid, YARAPI Norian acid, uni-PERIN acid, AMBURETTORU acid, ARYURITTO acid, 2-hydroxyoctedecenoic acid, 12-hydroxyoctadecanoic acid, 18-hydroxyoctadecanoic acid, 9,10-dihydroxyoctadecenoic acid,

Oxygensted fatty acid, auch as recinoleic acid, cam ROREN acid, licanic acid, ferron acid, and cerebronic acid; a halogenation object of monocarboxylic acid, such as chloracetic acid, 2-chlorocrylic acid, and chlorobenzoic acid, etc. are mentioned. As aliphatic dicarboxylic acid, adipic acid, szelaic acid, pimelic acid, Saturation dicarboxylic acid, such as SUPERIN acid, sebacic acid, ethylmalonic acid, glutaric acid, oxalic acid, malonic acid, succinic acid, and oxydiacstic acid; unsaturated dicarboxylic acid, such as maleic acid, fumario acid, acatylana dicarboxylic acid, and itaconic acid, etc. are mentioned. As aliphatic polycarboxylic acid, tricarboxylic acid, such as aconitic acid, citrate, and isocitric acid, etc. are mentioned. As aromatic carboxylic acid, benzoic acid, 9-anthracene carboxylic acid, Aromatic monocarboxylic acids, such as atrolactinic acid, anisic acid, isopropylbenzoic acid, salicylic acid, and toluic acid; aromatic polycarboxylic acids, such as phthalic acid, isophthalic acid, terephthalic acid, carboxyphenyl acetic acid, and pyromellitic acid, etc. are mentioned. In addition, amino acid, such as an alanine, leucine, threonine, aspartic acid, glutamic acid, arginine, cystein, methionine, phenylalanine, tryptophan, and histidine. is mentioned.

[0161]

Especially acquisition is easy, and is cheap and a point that compatibility with an ingredient (A1) is good to said carboxylic acid has 2-ethylhexanoic acid, octylic acid, neo decanoic acid, oleic acid, or preferred naphthenic acid.

[0162]

when the melting point of said carboxylic acid is high (crystallinity is high), the melting point becomes high in a similar manner, and it is hard to deal with carboxylic acid tin salt which has the acid radical (workability — bad). Therefore, as for the melting point of said carboxylic acid. it is preferrad that it is 65 ** or less, it is more prafarrad that it is -50-50 **, and it is preferred that it ia especially -40-35 **.

[0163]

when a carbon number of said carboxylic acid is large (a molecular weight is large), it becomes liquefied and carboxylic acid tin salt which has the acid radical becomes a thing which has a high solid state or viscosity and which is hard to deal with it (workability — bad). On the contrary, when a carbon number of said carboxylic acid is small (a molecular weight is small), catalyst ability of carboxylic acid metal salt may fall [carboxylic acid tin salt which has the acid radical], including mostly an ingredient which volatilizes easily with heating. Especially on conditions (thin layer) which extended a constituent thinly, volatilization by heating may be large and catalyst ability of carboxylic acid metal salt may fall greatly. Therefore, as for said carboxylic acid, it is preferred that carbon numbers including carbon of a carbonyl group are 2-20, it is more preferred that it is 6-17, and it is preferred that it is especially 8-12.

[0164]

It is preferred that it is the tin salt of a point of the ease (workability, viscosity) of dealing with it of carboxylic acid tin salt to dicarboxylic acid or monocarboxylic acid. and it is more preferred that it ia tha tin salt of monocarboxylic acid.

[0165]

As said monocarboxylic acid tin salt, it is a general formula (17). :

$Sn(OCOR)_2$ (17)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group. and may include a carbon carbon double bond.) Two RCOO-bases may be the same and may differ. A divalent Sn compound expressed or general formula (18) :

$Sn(OCOR)_4$ (18)

(It is the same as the above the inside R of a formula.) Two RCOO-bases may be the same and may differ. A tetravalent Sn compound expressed is preferred. A divalent Sn compound expressed with a general formula (17) from a point of hardenability and availability is more preferred.

[0166]

carboxylic acid tin salt (neo decanoic acid tin.) in which said carboxylic acid tin salt (C) is carboxylic acid tin salt (2-ethylhexanoic acid tin etc.) and the 4th class carbon whose carbon of an alpha position of a carboxyl group is the 3rd class carbon Pivalic-acid tin etc. are more preferred from a cura rate baing quick, and especially carboxylic acid tin salt whose carbon atom which adjoins a carbonyl group is tha 4th class carbon is preferred.

[0167]

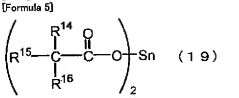
Especially in this invention. carbon of an alpha position of a carboxyl group uses carboxylic acid tin salt which is the 4th class carbon as an ingredient (C1) in carboxylic acid tin salt (C).

[0168]

(C1) As carboxylic acid tin salt of an ingradiant, it is a general formula (19). :

[0169]

[Formula 5]



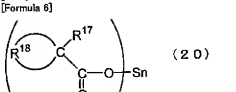
(19)

[0170]

(among the formula, R^{14}, R^{15}, and R^{16} are the independent substitution or unsubstituted univalent organic groups, respectively, and may contain the carboxyl group.) — the chain fatty acid tin expressed or general formula (20):

[0171]

[Formula 6]



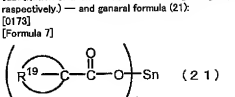
(20)

[0172]

(among the formula, an organic group univalent [substitution or unsubstituted] in R^{17} and R^{18} are substitution or unsubstituted divalent organic groups, and the carboxyl group may be included. respectively.) — and ganaral formula (21):

[0173]

[Formula 7]



(21)

[0174]

(among the formula, R^{19} is a substitution or unsubstituted trivalent organic group, and may contain the carboxyl group.) — cyclic-fatty-acid tin containing the structure expressed is mentioned. If the carboxylic acid which has an acid radical of carboxylic acid tin salt (C1) is illustrated concretely, A pivalic acid, 2,2-dimethylbutanoic acid, 2-ethyl-2-methylbutyric acid, 2,2-diethylbutanoic acid, A 2,2-dimethylvaleric acid, a 2-ethyl-2-methylvaleric acid, a 2,2-diethylvaleric acid, 2,2-dimethylhexana acid, 2,2-diethylhexanoic acid, 2,2-dimethyloctanoic acid, 2-ethyl-2.5-dimethylhexane acid, neo decanoic acid, BASA tio acid, Chain monocarboxylic acid, such as 2,2-dimethyl- 3-hydroxypropionic acid, Dimethylmalonic acid, ethyl methylmalonic acid, diethylmalonic acid, 2,2-dimethyl amber acid. Chain dicarboxylic acid, such as 2,2-diethyl amber acid and 2,2-dimethylglutaric acid, Chain

tricarboxylic acid, such as 3-methylisо citrate and 4,4-dimethylaconitic acid, 1-methylcyclopentanecarboxylic acid, 1,2,2-trimethyl 1,3-cyclopentane dicarboxylic acid, 1-methylcyclohexane carboxylic acid, 2-methylbicyclo[2.2.1]-5- heptene-2-carboxylic acid, 2-methyl-7-oxabicyclo [2.2.1]-5-heptane-2-carboxylic acid, 1-adamantane carboxylic acid, Annular carboxylic acid, such as bicyclo[2.2.1] heptane- 1-carboxylic acid and bicyclo[2.2.2] octane- 1-carboxylic acid, etc. are mentioned. These can also be used although many compounds containing such a structura to a natural product exist.

[0175]

From a point that compatibility with an ingredient and workability are especially (A1) good, tin monocarboxylate is more preferred and also chain tin monocarboxylate is more preferred. Since acquisition is easy, pivalic-acid tin, neo decanoic acid tin, BASA tic acid tin, 2,2-dimethyloctanoic acid tin, especially 2-ethyl-2,5-dimethylhexane acid tin, etc. are preferred.

[0176]

(C1) Also in an ingredient, although carboxylate of divalent tin and carboxylate of tetravalent tin are mentioned like a case of the above-mentioned (C) ingredient, carboxylate of a point of hardenability and availability to divalent tin is more preferred.

[0177]

As for a carbon number of carboxylic acid which has an acid radical of an ingredient (C1), it is preferred that it is 5-20, it is more preferred that it is 6-17, and it is preferred that It is especially 8-12. Since compatibility with an ingrediant may fall that it is easy to become a solid state (A1) and catalytic activity may fall if a carbon number inoreases more than this range, it is not desirable. It is not desirable from on the other hand, volatility, the increase of a smell, and the thin layer hardenability of a hardenability constituent falling, if there are few carbon numbers.

[0178]

As an ingredient, from these points (C1) Neo decanoic acid tin (divalent), BASA tic acid tin (divalent), 2,2-dimethyloctanoic acid tin (divalent), 2-ethyl-2,5-dimethylhexane acid tin (divalent), Neo decanoic acid tin (tetravalence), BASA tic acid tin (tetravalence), 2,2-dimethyloctanoic acid tin (tetravalence), and especially 2-ethyl-2,5-dimethylhexane acid tin (tetravalence) are preferred.

[0179]

(C) As amount of an ingredient and (C1) ingredient used, about 0.01-20 weight sections are preferred to ingredient (A1) 100 weight section, and also about 0.5-10 weight sections are preferred. Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings are less than this range, it is not desirable. On the other hand, if loadings exceed this range, working life becomes short too much, and workability may worsen, and it is not desirable from a point of storage stability.

[0180]

The (C) ingredient and (C1) an ingredient can be used combining two or more sorts besides using it alone.

[0181]

On the other hand, only of the (C) ingredient and (C1) an ingredient, activity is low, and when moderate hardenability is not acquired, an amine compound can be added as a co-catalyst.

[0182]

As various amine compounds, although indicated to JP,H5-287187,A, for example, Specifically Methylamine, ethylamine, propylamine, isopropylamine, A butylamine, amyl amine, hexylamine, octylamine, 2-ethylhexylamine, Nonyl amine, decyl amine, lauryl amine, pentadecyl amine, Aliphatic series primary amines, such as Sept iles amine, stearylamine, and cyclohexylamine; Dimethylamine, Diethylamine, dipropyl amine, diisopropylamine, dibutyl amine, Diamylamine, dioctyl amine, di(2-ethylhexyl) amine, Didecyl amine, dilauryl amine, JISECHIRU amine, distearyl amine, Aliphatic series secondary amines, such as methylstearylamine, ethylstearylamine, and butylstearylamine; Triethylamine, Aliphatic series tertiary amines, such as triamylamine, trihexyl amine, and trioctylamine; Triaryl amine, Aliphatic series unsaturation amines, such as oleylamine; aromatic-amine; Lauryl aniline, stearylaniline, a triphenylamine, N,N-dimethylaniline, dimethylbenzyl aniline, etc. reach, As other amines, monoethanolamine, diethanolamine, Triethanolamine, dimethylamino ethanol, diethylenetriamine, Triethylenetetramine, tetraethylenepantamine, benzylamine, Diethylamino propylamine, xylylene diamine, ethylenediamine, Hexamethylenediamine, dodecamethylenediamine,

dimethylethylenediamine, Triethylenediamine, guanidine, diphenylguanidine, N,N,N', and N"-tetramethyl 1,3-butanediamine, N,N,N', N"-tetramethyl ethylene diamine, 2,4,6-tris(dimethyl aminomethyl) phanol, Although morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene 7 (DBU) etc. are mentioned, it is not limited to these.

[0183]

As for loadings of said amine compound, about 0.01-20 weight sections are preferred to organic polymer 100 weight section of an ingredient (A1), and also ita 0.1 to 5 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 20 weight sections, pot life may become short too much and is not preferred from a point of workability.

[0184]

In this invention, an organic tin catalyst can be used as a (D) ingredient. When this organic tin catalyst is used as a silanol condensation catalyst of an organic polymer which has a reactive silicon group, as compared with other silanol condensation catalysts, a hardenability constituent with high catalytic activity, and good depths hardenability and an adhesive property is obtained. However, according to an addition of this organic tin catalyst, the stability of a hardened material of a hardenability constituent obtained, endurance, and creep resistance fall.

[0185]

A hardenability constituent which added an organic tin catalyst of the (D) ingredient by using an organic polymer which is an ingredient (A1) of this invention as a polymer component, Catalytic activity is high, and depths hardenability and an adhesive property are good, and the stability of a hardened material obtained, endurance, and creep resistance can be maintained highly.

[0186]

In using adhesives or a sealing material which, on the other hand, contains an organic polymer which has a reactive silicon group as the main ingredients for a use which needs endurance, it uses carboxylic acid tin salt of the aforementioned (C) ingredient as a curing catalyst in many cases. however, if this carboxylic acid tin salt is used as a curing catalyst, when it will be alike around a masonry joint and a sealing material will remain by a thin layer, it is hard to harden that thin layer portion, and may remain on conditions of heat and high humidity especially with un-hardening. On the other hand, if said organic tin catalyst (D) is used as a curing catalyst, as mentioned above, stability and endurance will fall, but the hardenability of a thin layer part is good. Then, if an organic tin catalyst of an organic polymer and the (D) ingredient which is an ingredient (A1) of this invention is combined, the hardenability of a thin layer part can be improved notably, maintaining the stability of a hardened material obtained, and endurance highly.

[0187]

However, even if it combinas with an organic polymer which is an ingradient (A1) of this invention, depending on an addition of an organic tin catalyst of the (D) ingredient, stability and endurance may fall a little. Then, it is more preferred to decrease the quantity of an addition of the (D) ingredient to such an extent that carboxylic acid tin salt of the (C) ingredient is used together and sufficient hardenability, depths hardenability, an adhesive property, and thin layer hardenability are acquired with an organic tin catalyst of the (D) ingredient as a curing catalyst.

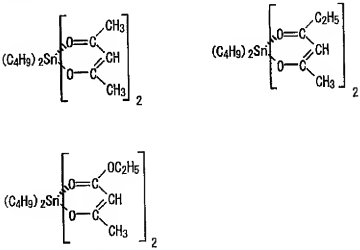
[0188]

As an example of said organic tin catalyst (D), they are dialkyl tin carboxylate, dialkyl tin oxide, and a general formula (22), :

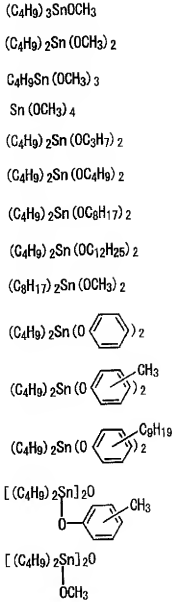
$Q_4Sn(OZ)_{4-g}$ or $[Q_4Sn(OZ)]_2O$ (22)

(Z expresses among a formula an organic group which has a functional group with which Q can form a coordinate bond in an inside of a univalent hydrocarbon group of the carbon numbers 1-20, or self for a univalent hydrocarbon group of the carbon numbers 1-20 to Sn.) g is 0, 1, 2, or 3. A compound etc. which are shown are shown. Tetravalent tin compounds, such as dialkyl tin oxide and dialkyl tin diacetate, It is usable as a (D) ingredient also in a reactant with a low molecula silicon compound which has hydrolytic silicon groups, such as a tetraethoxysilane, methyl triethoxysilane, diphenyldimethoxysilane, and phanyltrimethoxysilane. Since activity as a silanol condensation catalyst is high, chelate compound and tin alcoholates, such as a compound shown by a general formula (22) also in these, i.e., dibutyl tin bisacetylacetonate etc., are more preferred.

[0189]
As an example of said dialkyl tin carboxylate, For example, dibutyltin dilaurate, dibutyltin diacetate, a dibutyl tin diethylhexano rate, Dibutyl tin JIOKUTETO, dibutyl tin dimethylmalate, dibutyl tin diethyl malate, Dibutyl tin dibutyl maleate, dibutyl tin diisooctyl malate, Dibutyl tin ditridecyl malate, dibutyl tin dibenzyl malate, dibutyltin maleate, dioctyl tin diacetate, dioctyl tin distearate, dioctyl tin dilaurate, dioctyl tin diethyl malate, dioctyl tin diisooctyl malate, etc. are mentioned.
[0190]
As an example of said dialkyl tin oxide, dibutyl tin oxide, dioctyl tin oxide, a mixture of dibutyl tin oxide and phthalic ester, etc. are mentioned.
[0191]
If said chelate compound is illustrated concretely,
[0192]
[Formula 8]



[0193]
Although ** is mentioned, it is not limited to these. In these, its catalytic activity is high, and it is low cost, and since dibutyl tin bisacetylacetonate is easy to receive, it is the most preferred.
[0194]
If said tin alcoholates are illustrated concretely,
[0195]
[Formula 9]



[0196]
Although ** is mentioned, it is not limited to these. In these, a dialkyl tin JIARUKOKI side is preferred. Especially the dibutyl tin JIMETOKI side is low cost, and since it is easy to receive, it is

preferred.
[0197]
(D) As amount of ingradient uaed, about 0.01–20 weight sactions are preferred to ingradient (A1) 100 weight section, and also about 0.1–10 weight aactions are preferred. Since a cure rate may become slow and a hardening reaction will bacome fully difficult to advance if loadings are lesa than this range, it is not desirable. On the other hand, if loadings exceed this range, working life becomes short too much, and workability may worsen, and it is not desirable from a point of storage stability.
[0198]
As amount of [in case used of using the (D) ingredient and the (C) ingredient together as a curing catalyst], (A1) it is preferred to consider it as (C) ingredient:0.5 – 20 weight section and (D) ingredient:0.01 – 10 weight section to ingredient 100 weight section, and also it is more preferred to consider it as (C) ingredient:1 – 10 weight section and (D) ingredient:0.02 – 5 weight section. (C) When loadings of an ingredient are less than this range, a cure rate may become slow, when loadings exceed this range, working life becomes short too much and workability may worsen. (D) The stability of a hardened material which will be obtained if an improvement effect of hardenability, depths hardenability, an adhesive property, and thin layer hardenability may not be enough if loadings of an ingredient are less than this range, and loadings exceed this range, endurance, and creep resistance may worsen.
[0199]
The (D) ingredient can be uaed combining two or more sorts besides using it alone.
[0200]
In this invention, a non–tin catalyst can be used as a (E) ingradient. This non–tin catalyst haa a function which improves the stability of a hardened material obtained, endurance, and creep resistance as compared with other silanol condensation catalysts, when it uses as a silanol condensation catalyst of an organic polymer which is an ingradient (A1) of this invention. A non–tin catalyst which is the (E) ingredient is an eco–friendly curing catalyst with high social needs.
[0201]
As a non–tin catalyst which is the (E) ingredient which can be used for this invention, although there is no restriction in particular, an organic metallic compound containing carboxylic acid, carboxylic acid metal salt other than carboxylic acid tin salt, organic sulfonic acid, alkyl acid phosphate and 3B fellows, and 4A group metal, etc. are illustrated.
[0202]
The various above–mentioned carboxylic acid which has an acid radical of carboxylic acid tin salt which is the (C) ingredient as carboxylic acid can be illustrated.
[0203]
As for said carboxylic acid, it is preferred like carboxylic acid tin salt (C) that carbon numbers including carbon of a carbonyl group are 2–20, it is more preferred that it is 6–17, and it is preferred that it is especially 8–12. A point to dicarboxylic acid or monocarboxylic acid of the case (workability, viscosity) of dealing with it of carboxylic acid is preferred, and monocarboxylic acid is more preferred. carboxylic acid (neo decanoic acid.) in which said carboxylic acid is carboxylic acid (2–ethylhexanoic acid etc.) and the 4th class carbon whose carbon of an alpha position of a carboxyl group is the 3rd class carbon A pivalic acid etc. are more preferred from a cure rate being quick, and especially carboxylic acid whose carbon atom which adjoins a carbonyl group is the 4th class carbon is preferred.
[0204]
Especially as carboxylic acid, 2–ethylhexanoic acid, neo decanoic acid, BASA tic acid, 2,2–dimethyloctanoic acid, and 2–ethyl–2,5–dimethylhexane acid are preferred from a point of availability, hardenability, and workability.
[0205]
As carboxylic acid metal salt other than said carboxylic acid tin salt, metal salt of the various above–mentioned carboxylic acid can be used conveniently.
[0206]
In carboxylic acid metal salt other than said carboxylic acid tin salt, carboxylic acid bismuth, Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, Carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel,

carboxylic acid cobalt, a carboxylic acid zirconium, and carboxylic acid cerium. From a high point, the activity of a catalyst is preferred and Carboxylic acid bismuth, carboxylic acid calcium, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, Carboxylic acid barium, carboxylic acid manganese, and a carboxylic acid zirconium are more preferred. Carboxylic acid bismuth, carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, and a carboxylic acid zirconium are still more preferred, and carboxylic acid bismuth, carboxylic acid iron, and carboxylic acid titanium are especially the most preferred.
[0207]
Carboxylic acid bismuth, carboxylic acid calcium, carboxylic acid vanadium, Carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, It is more desirable from a point with little coloring of a hardenability constituent obtained, and a point that the heat resistance of a hardened material and weatherability which are obtained are high, and carboxylic acid bismuth, carboxylic acid calcium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, and a carboxylic acid zirconium are still more preferred.
[0208]
It is more preferred that it is metal salt of a point of the case (workability, viscosity) of dealing with it of carboxylic acid metal salt to monocarboxylic acid.
[0209]
As said monocarboxylic acid metal salt, it is general formula (23) – (35). :
$Bi(OCOR)_3$ (23)
$Ca(OCOR)_2$ (24)
$V(OCOR)_3$ (25)
$Fe(OCOR)_2$ (26)
$Fe(OCOR)_3$ (27)
$Ti(OCOR)_4$ (28)
$K(OCOR)$ (29)
$Ba(OCOR)_2$ (30)
$Mn(OCOR)_2$ (31)
$nickel(OCOR)_2$ (32)
$Co(OCOR)_2$ (33)
$Zr(O)(OCOR)_2$ (34)
$Ca(OCOR)_3$ (35)
(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.) Two ROOO–bases may be the same and may differ. Carboxylic acid metal salt expressed is preferred.
[0210]
As a carboxylic acid group of carboxylic acid metal salt other than said carboxylic acid tin salt, an acid radical of various carboxylic acid tin salt illustrated as the aforementioned (C) ingredient can be mentioned.
[0211]
From a viewpoint of the availability of a raw material, and compatibility, as an example of desirable carboxylic acid metal salt, 2–ethylhexanoic acid bismuth (trivalent), 2–ethylhexanoic acid iron (divalent), 2–ethylhexanoic acid iron (trivalent), 2–ethylhexanoic acid titanium (tetravalence), 2–ethylhexanoic acid vanadium (trivalent), 2–ethylhexanoic acid calcium (divalent), 2–ethylhexanoic acid potassium (univalent), 2–ethylhexanoic acid barium (divalent), 2–ethylhexanoic acid manganese (divalent), 2–ethylhexanoic acid nickel (divalent), 2–ethylhexanoic acid cobalt (divalent), 2–ethylhexanoic acid zirconium (tetravalence), 2–ethylhexanoic acid cerium (trivalent), neo decanoic acid bismuth (trivalent), Neo decanoic acid iron (divalent), neo decanoic acid iron (trivalent), neo decanoic acid titanium (tetravalence), Nao decanoic acid vanadium (trivalent), nao decanoic acid calcium (divalent), Neo decanoic acid potassium (univalent), neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence), Neo decanoic acid cerium (trivalent), bismuth oleate

(trivalent), oleic acid iron (divalent), oleic acid iron (trivalent), oleic acid titanium (tetravalence), oleic acid vanadium (trivalent), Oleic acid calcium (divalent), oleic acid potassium (univalent), oleic acid barium (divalent), Manganese oleate (divalent), oleic acid nickel (divalent), oleic acid cobalt (divalent), An oleic acid zirconium (tetravalence), oleic acid cerium (trivalent), naphthanic acid bismuth (trivalent), Naphthenic acid iron (trivalent), naphthenic acid iron (trivalent), naphthenic acid titanium (tetravalence), Naphthenic acid vanadium (trivalent), calcium naphthenate (divalent), naphthenic acid potassium (univalent), Naphthenic acid barium (divalent), manganese naphthenate (divalent), naphthenic acid nickel (divalent), cobalt naphthenate (divalent), a naphthenic acid zirconium (tetravalence), naphthenic acid cerium (trivalent), etc. are mentioned.

[0212]

2-ethylhexanoic acid bismuth (trivalent) from a viewpoint of catalytic activity. 2-ethylhexanoic acid iron (divalent), 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid titanium (tetravalence), Neo decanoic acid bismuth (trivalent), neo decanoic acid iron (divalent), neo decanoic acid iron (trivalent), Neo decanoic acid titanium (tetravalence), bismuth oleate (trivalent), oleic acid iron (divalent), Oleic acid iron (trivalent), oleic acid titanium (tetravalence), naphthenic acid bismuth (trivalent), Naphthenic acid iron (divalent), naphthenic acid iron (trivalent), and naphthenic acid titanium (tetravalence) are more preferred, and 2-ethylhexanoic acid iron (trivalent), neo decanoic acid iron (trivalent), and especially naphthenic acid iron (trivalent) are preferred.

[0213]

2-ethylhexanoic acid bismuth (trivalent) from a viewpoint of coloring, 2-ethylhexanoic acid titanium (tetravalence), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid zirconium (tetravalence), Neo decanoic acid bismuth (trivalent), neo decanoic acid titanium (tetravalence), Neo decanoic acid calcium (divalent), neo decanoic acid potassium (univalent), Neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence), Bismuth oleate (trivalent), oleic acid titanium (tetravalence), oleic acid calcium (divalent), Oleic acid potassium (univalent), oleic acid barium (divalent), an oleic acid zirconium (tetravalence), Naphthenic acid bismuth (trivalent), naphthenic acid titanium (tetravalence), calcium naphthenate (divalent), naphthenic acid potassium (univalent), naphthenic acid barium (divalent), and a naphthenic acid zirconium (tetravalence) are more preferred.

[0214]

Toluenesulfonic acid, styrene sulfonic acid, etc. are raised as organic sulfonic acid.

[0215]

Alkyl acid phosphate is $-O-P(=O)OH$. It is phosphoric ester containing a portion and alkyl acid phosphate as shown below is contained. An organic acid nature phosphoric ester compound is preferred in respect of compatibility and curing catalyst activity.

[0216]

An organic acid nature phosphoric ester compound is expressed with $_h(R^{20}-O)-P(=O)(-OH)_{3-h}$ (in the inside h of a formula, 1 or 2, and R^{20} show an organic residue).

[0217]

Below, it illustrates concretely.

$(CH_3O)_2-P(=O)(-OH)$, $(CH_3O)-P(=O)(-OH)_2$, $(C_2H_5O)_2-P(=O)(-OH)$, $(C_2H_5O)-P(=O)(-OH)_2$ and $_2(C_3H_7O)-P(=O)(-OH)$, $(C_3H_7O)-P(=O)(-OH)_2$ and $_2(C_4H_9O)-P(=O)(-OH)$, $(C_4H_9O)-P(=O)(-OH)_2$ and $_2(C_8H_{17}O)-P(=O)(-OH)$, $(C_8H_{17}O)-P(=O)(-OH)_2$, $(C_{10}H_{21}O)_2-P(=O)(-OH)$, $(C_{10}H_{21}O)-P(=O)(-OH)_2$, $(C_{13}H_{27}O)_2-P(=O)(-OH)$, $(C_{13}H_{27}O)-P(=O)(-OH)_2$ and $_2(C_{16}H_{33}O)-P(=O)(-OH)$, $(C_{16}H_{33}O)-P(=O)(-OH)_2$, $(HO-C_6H_{12}O)_2-P(=O)(-OH)$, $(HO-C_6H_{12}O)-P(=O)(-OH)_2$, $(HO-C_8H_{16}O)-P(=O)(-OH)$, $(HO-C_8H_{16}O)-P(=O)(-OH)_2$, $[(CH_2\ OH)(CHOH)O]_2-P(=O)(-OH)$, $[(CH_2\ OH)(CHOH)O]-P(=O)(-OH)_2$ etc. are raised, it is not limited to the above-mentioned illustration substance.

[0218]

By carboxylic acid, carboxylic acid metal salt other than carboxylic acid tin salt, organic sulfonic acid, and alkyl acid phosphate, activity is low, and when moderate hardenability is not acquired, an amine

compound can be added as a co-catalyst.

[0219]

As various amine compounds, the indicated various above-mentioned amine compounds can be used as a co-catalyst of carboxylic acid tin salt (C).

[0220]

As for loadings of said amine compound, about 0.01-20 weight sections are preferred to organic polymer 100 weight section of an ingredient (A1), and also its 0.1 to 5 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 20 weight sections, pot life may become short too much and is not preferred from a point of workability.

[0221]

As a metal system compound of non-tin, besides carboxylic acid metal salt other than said carboxylic acid tin salt, An organic metallic compound containing 3B fellows and 4A group metal is raised, and although a titanate organic compound, an organoaluminum compound, an organic zirconium compound, an organic boron compound, etc. are preferred from a point of activity, it is not limited to these.

[0222]

As said titanate organic compound, tatraisopropyl titanate, Tetrabuthyl titanate, tetramethyl titanate, tetra (2-ethylhexyl titanate), Chelate compound, such as titanium chelate, such as titanium alkoxides, such as triethanolamine titenate, titanium tetra acetylacetoneto, titanium ethylacetoacetate, octylene glycolate, and titanium lactate, etc. are raised.

[0223]

As said organoaluminium compound, aluminum isopropylate, Aluminum alkoxides, such as mono sec-butoxy aluminum diisopropylate and aluminum sec-butyrate. Aluminum chelate, such as aluminum tris acetylacetoneto, aluminumtrisethylacetoacetate, and diisopropoxy aluminum ethylacetoacetate, is raised.

[0224]

As said zirconium compound, zirconium tetra isopropanal POKISAIDO, Zirconium alkoxides, such as a zirconium tetra-n PUROPI rate and zirconium normal butyrate. Zirconium chelate, such as zirconium tetra acetylacetonato, zirconium monoacetyl acetonate, zirconium bisacetylacetonate, zirconium acetylacetonato bis-ethylacetoacetate, and zirconium acetate, is raised.

[0225]

Although **** concomitant use is also possible so, these titanate organic compounds, an organoaluminium compound, an organic zirconium compound, an organic boron compound, etc., It is desirable in a viewpoint which can reduce the amount of catalyst used especially according to concomitant use with said amine compound or an alkyl-acid-phosphate compound since it is possible to improve activity, and more desirable in a viewpoint of adjustment of working life in hardenability and ordinary temperature in an elevated temperature.

[0226]

(E) As amount of ingredient used, about 0.01-20 weight sections are preferrad to ingredient (A1) 100 weight section, and also about 0.5-10 weight sections are preferred. Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings are less than this range, it is not desirable. On the other hand, if loadings exceed this range, working life becomes short too much, and workability may worsen, and it is not desirable from a point of storage stability.

[0227]

The (E) ingredient can be used combining two or more sorts besides using it alone.

[0228]

In this invention, a minute hollow body can be used as a (F) ingredient. While improving the workability (********, thixotropy) of a constituent notably as indicated to JP,H11-35923,A or JP,H11-310772,A if this minute hollow body is used, it is known that a weight saving of a constituent and low-cost-izing are possible. However, it is known that the stability of a hardened material of a hardenability constituent and endurance which are obtained will fall according to an addition of this minute hollow body.

[0229]

The hardenability constituent which added a minute hollow body of the (F) ingredient by using an organic polymer which is an ingredient (A1) of this invention as a polymer component can maintain highly the stability of a hardened material and endurance which are obtained, improving workability (********) notably.

[0230]

a very small hollow body (henceforth a balloon) which is the (F) ingredient of this invention is a hollow body by which a diameter was preferably constituted from material of minerals of 500 micrometers or less or quality of organicity 1 mm or less as indicated, for example on "state-of-the-art art of a functional filler" (CMC). (F) An ingredient in particular is not limited but it is [ingredient] usable in various kinds of publicly known balloons.

[0231]

As for average particle density of a balloon, it is preferred that it is 0.01 – 1.0 g/cm^3, it is more preferred that it is 0.03 – 0.7 g/cm^3, and it is preferred that it is especially 0.1 – 0.5 g/cm^3. If tensile strength of a hardened material may fall if average particle density is less than this range, and average particle density exceeds this range on the other hand, a workability improvement effect may not be enough.

[0232]

An inorganic system balloon is more preferred than a point of stability and endurance to an organic system balloon.

[0233]

As said inorganic system balloon, can illustrate a silicic acid system balloon and a non-silicic acid system balloon, and on a silicic acid system balloon. A milt balloon, perlite, glass balloons, a silica balloon, fly ash balloons, etc. can illustrate an alumina balloon, a zirconia balloon, a carbon balloon, etc. on a non-silicic acid system balloon. As an example of these inorganic system balloons, as a milt balloon, a win light by IJICHI Chemicals, As a SANKI light by Sanki Engineering Co., Ltd., and glass balloons, KARUN by Nippon Sheet Glass Co., Ltd., The Sumitomo 3M cell star Z-28, MICRO BALLOON made from EMERSON&CUMING, CELAMIC GLASSMODULES made from PITTSBURGE CORNING, As GLASS BUBBLES made from 3M, FUJIBA lune made from Fuji SHIRISHIA Chemicals, and a silica balloon, as Q-CEL by Asahi Glass Co., Ltd., SAIRISHIA made from Fuji SHIRISHIA Chemicals, and fly ash balloons, CEROSPHERES made from PFAMARKETING, FILLITE made from FILLITE U.S.A, As an alumina balloon, as BW by Showa Denko K.K., and a zirconia balloon HOLLOW ZIRCONIUM SPHEES made from ZIRCOA, KUREKASU fair made from Kureha Chemicals and product car boss fair made from GENERAL TECHNOLOGIES are marketed as a carbon balloon.

[0234]

A balloon of thermosatting resin and a balloon of thermoplastics can be illustrated as said organic system balloon, On a thermosetting balloon, a phenol balloon, an epoxy balloon, and a urea balloon can illustrate a saran balloon, a polystyrene balloon, a polymethacrylate balloon, a polyvinyl alcohol balloon, and a styrene acrylic balloon at a thermoplastic balloon. A balloon of thermoplastics which constructed the bridge can also be used. A balloon after foaming may be sufficient, and a balloon here is made to foam, after blending a thing containing a foaming agent, and is good also as a balloon.

[0235]

As an example of these organic system balloons, as a phenol balloon, Union Carbide UCAR and PHENOLIC MICROBALLOONS, As an epoxy balloon, ECOSPHERES made from EMERSON&CUMING, As a urea balloon, ECOSPHERES VF-O made from EMERSON&CUMING, As a saran balloon, SARAN MICROSPHERES made from DOW CHEMICAL, Expancel made from Japanese Filament, the Matsumoto Yushi-Seiyaku Matsumoto microsphere, As a polystyrene balloon, DYLITE EXPANDABLE POLYSTYRENE made from ARCO POLYMERS, SX863 by Japan Synthetic Rubber Co., Ltd. (P) are marketed by EXPANDABLE POLYSTYRENE BEADS made from BASF WYANDOTE, and constructed type styrene acrylic acid balloon of a bridge.

[0236]

The above-mentioned balloon may be used alone, and two or more kinds may be mixed and it may be used. The surface of these balloons Fatty acid, fatty acid ester, rosin, What was processed in order to improve dispersibility and the workability of a compound by rosin acid lignin, a silane coupling agent, titanium coupling agent, aluminum cup ring agent, a polypropylene glycol, etc. can be used. Without spoiling pliability, and elongation and intensity among physical properties at the time of

stiffening a compound, these balloons are used in order to carry out a weight saving and to cut down the cost.

[0237]

As for the amount of balloon used, about 0.1–50 weight sections are preferred to ingredient (A1) 100 weight section, and also its about 0.5–30 weight sections are preferred. When a workability improvement effect may not be enough if loadings are less than this range, and loadings exceed this range, tensile strength of a hardened material may fall or stability and endurance may worsen.

[0238]

At this invention, it is a general formula as a (G) ingredient (7). :

– $SiR^5_c(OR^6)_{3-c}$ (7)

(Among a formula, c R^5 is the organic groups of monovalence of the carbon numbers 1–20 independently, and 3–c R^6, respectively) It is an organic group of monovalence of the carbon numbers 2–20 independently, and c shows 0, 1, or 2, respectively. An aminosilane coupling agent which has a basis expressed can be used. General formula (6) which is the (A4) ingredient of this invention about this (G) ingredient :

– $Si(OR^4)_3$ (6)

While having stability, endurance, and creep resistance outstanding by adding to an organic polymer which has a basis expressed with (R^4 in a formula is the same as the above), it becomes a hardenability constituent in which an outstanding adhesive property is shown. To a reactive silicon group of this (G) ingredient. Even if an ester exchange reaction between reactive silicon groups of the (G) ingredient and the (A4) ingredient advances after mixing with the (A4) ingredient since it does not have a methoxy group as an alkoxy group combined with a silicon atom, a reactant high methoxy silyl group does not generate to a reactive silicon group of the (A4) ingredient. Therefore, a hardenability constituent containing the (G) ingredient and the (A4) ingredient is before and after storage, and turns into a hardenability constituent with little change of a cure rate. A reactive silicon group of this (G) ingredient and the (A4) ingredient. Since a carbon number of an alkoxy group combined with a silicon atom is 2 to 20, toxic high methanol is not contained in alcohol generated in connection with a hydrolysis reaction of a reactive silicon group when a hardenability constituent carries out condensation hardening, but becomes it with a constituent with high safety.

[0239]

(G) Although it is usable as a many liquid [, such as 1 liquid type and a two-component type,] type constituent, when it is considered as 1 liquid type, since said hardenability constituent which consists of an ingredient and a (A4) ingredient has a large effect which makes small especially change of a cure rate in storage order, it is preferred.

[0240]

(G) An ingredient is a compound which has a reactive silicon group expressed with a general formula (7), and an amino group. As an example of a reactive silicon group expressed with a general formula (7), a triethoxy silyl group, a methyldi ethoxy silyl group, a dimethylathoxy silyl group, an ethyldiethoxy silyl group, a triisopropoxy silyl group, a methyldi isopropoxy silyl group, etc. can be mentioned. An alkoxy group combined with a silicon atom of a reactive silicon group has preferred toxic ethoxy silyl group from a viewpoint or isopropoxy silyl of alcohol generated in connection with a hydrolysis reaction, and its ethoxy silyl group is more preferred. From a viewpoint of a cure rate, as for the number of an alkoxy group combined with one silicon atom of a reactive silicon group, two or more pieces are preferred, and its three pieces are more preferred. The toxicity of alcohol generated in connection with a hydrolysis reaction and a viewpoint of a cure rate to a triethoxy silyl group is the most preferred.

[0241]

As an example of an ingredient, (G) gamma-aminopropyl triethoxysilane, gamma-aminopropyl triisopropoxy silane, gamma-aminopropyl methyldiethoxysilane, gamma-(2-aminoethyl) aminopropyl triethoxysilane, gamma-(2-aminoethyl) aminopropyl triisopropoxy silane, gamma-(2-aminoethyl) aminopropyl mathyldiethoxysilane, gamma-ureido propyl triethoxysilane, gamma-ureido propyl trilsopropoxy silane, gamma-ureido propylmethyl diethoxyailane, N-phanyl-gamma-aminopropyl triethoxysilane, N-banzyl-gamma-aminopropyl triethoxysilane, N-n-butyl-gamma-aminopropyl triethoxysilane, N-vinylbanzyl gamma-aminopropyl triethoxysilane, N,N'-bis[gamma-triethoxy silyl

propyl)ethylenediemine, Amino group content Silang, such as bis(triethoxy silyl propyl)amine and gamma-[2-(2-aminoethyl) aminoethyl] aminopropyl triethoxysilane, can be mentioned. A denatured derivative and a condensation reaction thing of the above-mentioned silane compound can also use the above-mentioned silane compound as a (G) ingredient.

[0242]

The (G) ingredient used for this invention is used in 0.1-10 copies to 100 copies of organic polymers of the (A4) ingredient. It is preferred to use it in 1-5 copies especially. The above-mentioned (G) ingredient may be used only by one kind, and may carry out two or more kind mixing use.

[0243]

(A4) A dehydrator may be added when using as a 1 liquid type constituent a constituent which consists of an ingredient and a (G) ingredient. Especially as said dehydrator, it is not restricted but various kinds of compounds can be used. Since [that a change in physical properties after a silicon compound which has alkoxy silyl groups and does not contain an amino group as a dehydrator storing by care of health at low temperature comparatively since an ester exchange reaction with a reactive silicon group of the (A4) ingredient is late is small and] the drying effect is high, it is desirable. Since a silicon compound which has the Tori alkoxy silyl groups and does not contain an amino group has the higher drying effect, it is preferred, and especially a silicon compound that has a trimethoxysilyl group and does not contain an amino group is preferred. Specifically, alkyltrialkoxysilane, such as vinyltrimetoxysilane, methyl trimetoxysilana, and phenyltrimethoxysilane, is preferrad from points, such as the drying effect, hardenability, availability, and the tension physical properties of a hardened material.

[0244]

At this invention, it is a general formula as a (H) ingredient (8). :

$$-SiR^7_d(OCH_3)_{3-d-e}(OR^8)_e \quad (8)$$

(Among a formula, d R^7 is the organic groups of monovalence of the carbon numbers 1-20 independently, respectively. R^8 of a 3-d-e individual is an organic group of monovalence of the carbon numbers 2-20 independently, and d shows 0, 1, or 2 and, as for e, it shows 1, 2, or 3, respectively.) However, 3-d-e>=0 shall be satisfied. An aminosilane coupling agent which has a basis expressed can be used. General formula (6) which is the (A4) ingredient of this invention about this (H) ingredient :

$$-Si(OR^4)_3 \quad (6)$$

If it is recuperated beforehand, a hardenability constituent added to an organic polymer which has a basis expressed with (R^4 in a formula is the same as the above). (H) An ester exchange reaction between a methoxy silyl group of an ingredient and a reactive silicon group of the (A4) ingredient advances, and a reactant high methoxy silyl group generates to a reactive silicon group of the (A4) ingredient. A hardenability constituent obtained as a result turns into a hardenability constituent of fast curability while having outstanding adhesive property, stability, endurance, and creep resistance.

[0245]

(H) Desirable care-of-health conditions of said hardenability constituent which consists of an ingredient and a (A4) ingredient, Since it changes with existence of a transesterification catalyst and its addition, ester exchange reaction activity of a reactive silicon group of the (H) ingredient and the (A4) ingredient, etc., are not generally decided, but as a transesterification catalyst, When it includes an organic tin catalyst or 0.5 copy - about three copies of Ti system catalysts in a system, in a low temperature service, the 10-30 ** thing for which it is recuperated comparatively one week or more is preferred, and it is preferred that more than a day recuperates itself in not less than 30 ** high temperature service.

[0246]

(H) Although it is usable as a many liquid [, such as 1 liquid type and a two-component type,] type constituent, when it is considered as 1 liquid type, since said hardenability constituent which consists of an ingredient and a (A4) ingradient has a remarkable change of a cure rate especially by care of health, it is preferred.

[0247]

(H) An ingredient is a compound which hes a reactive silicon group expressed with a general formula (8), and an amino group. As an example of a reactive silicon group expressed with a general formula

(8), A trimethoxysilyl group, a methyl dimethoxy silyl group, an ethyl dimethoxy silyl group, an ethoxy dimethoxy silyl group, a dimethyl methoxy silyl group, a diethyl methoxy silyl group, a diethoxy methoxy silyl group, etc. can be mentioned. From a viewpoint of ester exchange reaction speed, as for the number of an alkoxy group combined with one silicon atom of a reactive silicon group, two or more pieces are preferred, and its three pieces are more preferrad. Therefore, a trimethoxysilyl group is the most preferred.

[0248]

As an example of an ingredient, (H) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl ethyl dimethoxysilane, gamma-aminopropyl ethoxy dimethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl ethyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl ethoxy dimethoxysilane, gamma-ureido propyltrimethoxysilane, gamma-ureido propylmethyl dimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, N-benzyl-gamma-aminopropyl trimethoxysilane, N-n-butyl-gamma-aminopropyl trimethoxysilane, N-vinylbenzyl gamma-aminopropyl trimethoxysilane, Amino group content Silang, such as N,N'-bis (gamma-trimethoxysilylpropyl)ethylenediamine, bis(trimethoxysilylpropyl)amine, and gamma-[2-(2-aminoethyl) aminoethyl] aminopropyl trimethoxysilane, can be mentioned. A denatured derivative and a condensation reaction thing of the above-mentioned silane compound can also use the above-mentioned silane compound as a (H) ingredient.

[0249]

The (H) ingredient used for this invention is used in 0.1-10 copies to 100 copies of organic polymers of the (A4) ingredient. It is preferred to use it in 1-5 copies especially. The above-mentioned (H) ingredient may be used only by one kind, and may carry out two or more kind mixing use.

[0250]

In this invention, an epoxy resin can be used as a (I) ingredient. This epoxy resin has a function which raises stability, endurance, and creep resistance further while improving impact strength and tough nature of an organic polymer which are the (A4) ingredients of this invention.

[0251]

As an epoxy resin used as a (I) ingredient of this invention, an epichlorohydrin bisphenol A type epoxy resin, Fire retardancy type epoxy resins, such as epichlorohydrin bisphenol F type epoxy resin and glycidyl ether of tetrabromobisphenol A, Novolak type epoxy resin, a hydrogenation bisphenol A type epoxy resin, A glycidyl ether type epoxy resin of a bisphenol A propylene oxide addition, p-oxybenzoic acid glycidyl ether ester typed epoxy resin, m-aminophenol series epoxy resin, A diaminodiphenylmethane system epoxy resin, a urethane modified epoxy resin, Various cycloaliphatic-epoxy-resin and N,N-diglycidyl aniline, N,N-diglycidyl o-toluidine, Although an epoxidation thing of an unsaturation polymer, etc. are illustrated at the time, such as glycidyl ether of polyhydric alcohol, e hydantoin type epoxy resin, and petroleum resin, at the time, such as triglycidyl isocyanurate, polyallylene glycol diglycidyl ether, and glycerin, Not a thing limited to these but an epoxy resin currently generally used is used, and it gets. What contains an epoxy group in [two] a molecule at least hae high reactivity when hardening, and a hardened material is preferred from points — it is easy to build three-dimensional meshes of a net. As a still more desirable thing, bisphenol A type epoxy resins or novolak type epoxy resin is raised. Ranges of a using rate of these epoxy resin (I) and reactive silicon group containing organic polymer (A4) are (A4)/epoxy resin =100 / 1 - 1/100 in a weight ratio, (A4) If the improvement effect of impact strength of an epoxy resin hardened material, tough nature, stability, endurance, and creep resistance becomes will be hard to be acquired if a rate of a /epoxy resin becomes less than 1/100 and a rate of (A4)/epoxy resin surpasses 100/1, intensity of an organic polymer hardened material will become insufficient. Since a desirable using rate changes with uses of a hardenability constituent, etc., are not generally decided, but. For example, when improving the shock resistance of an epoxy resin hardened material, flexibility, tough nature, peel strength, etc., it is good to carry out 5-100 weight-section use of the (A4) ingredient still more preferably as to 100 weight section to epoxy resin 100 weight section. On the other hand, when improving intensity of a hardened material of the (A4) ingredient, it is good to carry out 5-50 weight-section use of the epoxy resin five to 100 weight section still more preferably espacially one to 200 weight section to (A4) ingredient 100 weight section.

[0252]

Naturally a hardening agent which makes a constituent of this invention harden an epoxy resin can be used together. As an epoxy resin hardener which can be used, there is no restriction in particular and an epoxy resin hardener currently generally used can be used. Specifically, for example Triethylenetetramine, tetraethylenepentamine, Diethylamino propylamine, N-aminoethyl piperidine, m-xylylene diamine, m-phenylenediamine, diaminodiphanylmathane, diaminodiphenyl sulfone, The first classes, such as isophoronediamine and amine and polyether, second class amines;2,4,6-tris(dimethyl aminomethyl) phenol, The third class amines like tripropylamine. and the salts; polyamide resin; imidazole-derivatives; dicyandiamides of these third class amines; Boron trifluoride complex compounds. Phthalic anhydride, hexahydro phthalic anhydride, tetrahydro phthalic anhydride, Anhydrous carboxylic acid; alcohols; phenols; carboxylic acid, such as DODESHINIRU succinyl oxide, pyromellitic dianhydride, and anhydrous KUROREN acid; although compounds, such as a diketone complex compound of aluminum or a zirconium, can be illustrated, it is not limited to these. A hardening agent may also be independent or two or more sorts may be used together.
[0253]
When using a hardening agent of an epoxy resin, the amount used is the range of 0.1 to 300 weight section to epoxy resin 100 weight section.
[0254]
Ketimine can be used as a hardening agent of an epoxy resin. In the state where ketimine does not have moisture, it exists stably, and it is decomposed into primary amine and ketone by moisture, and produced primary amins aervas as a hardening agent of the room-temparature-ouring nature of an epoxy resin. If ketimine is used, a 1 liquid type constituent can be obtained. As such ketimine, it can obtain by a condensation reaction of an amine compound and a carbonyl compound.
[0255]
Although what is necessary is just to use a publicly known amine compound and a carbonyl compound for composition of ketimine, As an amine compound, for example, ethylenediamine, propylenediamine, Trimethylene diamine, a tetramethylenediamine, 1,3-diaminobutane, 2,3-diaminobutane, pentamethylene diamine, 2,4-diaminopentane, Diamine;1,2,3-triamino propane, such as hexamethylenediamine, p-phenylene diamine, and p,p'-biphenylene diamine, Multivalent amine, such as triamino benzene, tris(2-aminoethyl) amine, and tetra(aminomethyl) methane; Diethylenetriamine, Polyalkylene polyamine, such as TORIEGHIREN triamine and tetraethylenepentamine; Polyoxyalkylene series polyamine;gamma-aminopropyl triethoxysilane, Aminosilanes [, such as N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane and N-(beta-aminoethyl)-gamma-aminopropyl methyl dimethoxysilane,], etc. are used, and it gets. As a carbonyl compound, acetaldehyde, propionaldehyde, n-butylaldehyda, isobutyraldehyde, diethylacetaldehyde, Aldehyde, such as a glyoxal and benzaldehyde; Cyclopentanone, Cyclic ketone, such as trimethyl cyclopentanone, cyclohexanone, and trimethyl cyclohexanone; Acetone, Methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, Methyl isobutyl ketone, a diethyl ketone, dipropyl ketone, diisopropyl keton, Aliphatic series ketone, such as dibutyl ketone and diisobutyl ketone; beta-dicarbonyl compound [, such as an acetylacetone, methyl acetoacetate, ethyl acetoacetate, dimethyl malonate, diethyl malonate, a malonic acid methylethyl, and dibenzoylmethane,]; etc. can be used.
[0256]
When an imino group exists in ketimine, an imino group may be made to react to glycidyl ether; glycidyl ester, such as styrene oxide; butyl glycidyl ether and allyl glycidyl ether, etc. Such ketimines may be used independently, two or more kinds may be used together and used for them, 1-100 weight-section use is carried out to epoxy resin 100 weight section, and the amount used changes with kinds of an epoxy resin and ketimine.
[0257]
Various bulking agents other than a minute hollow body of the (F) ingredient may be blended with a hardenability constituent of this invention. It is not limited especially as said bulking agent, but For example, fumes silica, sedimentation nature silica, Reinforcement nature bulking agents, such as a silicic acid anhydride, hydrous silicic acids, and carbon black; Caloium carbonate, Bulking agents, such as magnasium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zino oxide, an active white, and hydrogenation castor oil; fibrous fillers, such as asbestoe, glass fiber, and a filament, are illustrated.
[0258]

To obtain a hardenability constituent with high intensity with these bulking agents. Mainly Fumes silica, sedimentation natura silica, a silicic acid anhydride, hydrous silicic acids, carbon black, A desirable result will be obtained if a bulking agent chosen from surface treatment detailed calcium carbonate, calcination clay, olay, an active white, etc. is used in the range of 1 - 100 weight section to organic polymer (A) 100 weight section. When elongation wants to obtain a hardenability constituent which is size with low strength, A desirable rasult will be obtained if a bulking agent mainly chosen from titanium oxide, calcium carbonate, magnesium carbonate, talc, ferric oxide, a zinc oxide, etc. is used in the range of 5 - 200 weight section to organic polymer (A) 100 weight section. Of course, these bulking agents may be used only by one kind, and may mix and use two or more kinds.
[0259]
In a hardenability constituent of this invention, since elongation of a hardened material can be enlarged or a lot of bulking agents can be mixed if a plasticizer is used, using it together with a bulking agent, it is more effective.
[0260]
As this plasticizer, dioctyl phthalate, dibutyl phthalate. Phthalic ester, such as butylbenzyl phthalate; Dioctyl adipate, Aliphatic dibasic acid ester, such as succinic acid isodecyl and dibutyl sebacate; Diethylene glycol dibenzoate, Glycol ester, such as pentaerythritol ester; Butyl oleate, Aliphatic series ester species, such as methyl acetyl ricinolate; Triceryl phosphate, Phosphoric ester, such as trioctyl phosphate and phosphoric acid octyldiphenyl; Epoxidized soybean oil, Polyether, such as polyester plasticizer; polypropylene glycols, such as polyester of epoxy plasticizer; dibasic acid and dihydric alcohol, such as epoxidation linseed oil and epoxy stearic acid benzyl, and a derivative of these; Polly alpha-methylstyrene, Polystyrene, such as polyatyrene; plasticizers, such as polybutadiene, Butadiene Acrylonitrile, polychloroprene, polyisoprene, polybutene, and chlorinated paraffins, can use it independently arbitrarily in a form of two or more kinds of mixtures. A desirable result will be obtained if the amount of plasticizers is used in 100 or less weight sections to organic polymer (A) 100 weight section.
[0261]
A polymeric plasticizer can be used. If a polymeric plasticizer is used, as compared with a case where a low molecule plasticizer which is a plasticizer which does not contain a polymer component in a molecule is used, early physical properties are maintained over a long period of time, and drying property (it is also called paintwork) at the time of applying an alkyd paint to this hardened material can be improved. A vinyl-base polymer produced by polymerizing by various methods in a vinyl system monomer as an example of a polymeric plasticizer; Diethylene glycol dibenzoate, Ester species of polyalkylene glycols, such as triethylene glycol dibenzoate and pentaerythritol ester; Sebacic acid, Dibasic acid and ethylene glycol, such as adipic acid, azelaic acid, and phthalic acid, A diethylene glycol, triethylene glycol, propylene glycol, A polyester plasticizer obtained from dihydric alcohol, such as dipropylene glycol; 500 or more molecular weights, Further 1000 or more polyethylene glycols, a polypropylene glycol, A hydroxyl group of polyether polyol, such as polytetramethylene glycol, or these polyether polyol An ester group, polyether [, such as a derivative changed into an ether group etc.,]; -- polystyrene [, such as polystyrene and Polly alpha-methylstyrene,], although polybutadiene, polybutene, polyisobutylene, butadiene acrylonitrile, polychloroprene, etc. are mentioned. It is not limited to these.
[0262]
Among these polymeric plasticizers, a polymer of the (A) ingredient and a thing to dissolve are preferred. Polyether and a vinyl-base polymer are preferred. A heat-resistant point to compatibility and weatherability, and a vinyl-base polymer are especially preferred. Also in a vinyl-base polymer, an acrylic polymer and/or an methacrylic system polymer are preferred, and acrylic polymers, such as polyacrylic acid alkyl ester, are still more preferred. Its molecular weight distribution is narrow, since hypoviscosity-izing is possible for a synthetic method of this polymer, it is preferred, and it is still more preferred. [of an atom-transfer-radical-polymerization method] [of a living-radical-polymerization method] It is preferred to use a polymer what is called by a SGO process which obtained an acrylic-acid-alkyl-ester system monomer indicated to JP,2001-207157,A by continuation mass polymerization with an elevated temparature and high voltage.
[0263]

although number average molecular weights of a polymeric plasticizer are 500-15000 preferably, they are 800-10000 more preferably — further — desirable — 1000-8000 — it is 1000-5000 especially preferably. It is 1000-3000 most preferably. If a molecular weight is too low, a plasticizer can flow out temporally by heat or a rainfall, early physical properties cannot be maintained over a long period of time, and alkyd paintwork cannot be improved. If a molecular weight is too high, viscosity will become high and workability will worsen. Although molecular weight distribution in particular of a polymeric plasticizer is not limited, a narrow thing is preferred and less than 1.80 are preferred. 1.70 or less are more preferred, in addition, 1.60 or less are preferred, 1.50 or less are still more preferred, 1.40 especially or less are preferred, and 1.30 or less are the most preferred.

[0264]

A number average molecular weight of a polymeric plasticizer and molecular weight distribution (Mw/Mn) are measured by the GPC method (polystyrene conversion).

[0265]

Although a polymeric plasticizer does not have a reactive silicon group, it may have a reactive silicon group. When it has a reactive silicon group, it acts as a reaction plasticizer and shift of a plasticizer from a hardened material can be prevented. When it has a reactive silicon group, it averages per molecule and one or less piece and 0.8 more piece or less are preferred. When using a plasticizer which has a reactive silicon group, especially an oxyalkylene polymer which has a reactive silicon group, the number average molecular weight needs to be lower than a polymer of the (A) ingredient.

[0266]

A plasticizer may be used alone and may use two or more sorts together. A low molecule plasticizer and a polymeric plasticizer may be used together. These plasticizers can also be blended at the time of polymer manufacture.

[0267]

The amount of plasticizer used is 20 - 100 weight section still more preferably ten to 120 weight section preferably five to 150 weight section to (A) ingredient 100 weight section. In less than five weight sections, if an effect as a plasticizer stops being revealed and 150 weight sections are exceeded, mechanical strength of a hardened material runs short.

[0268]

It is a general formula in order to improve the activity of a condensation catalyst more in a hardenability constituent of this invention. $R_aSi(OR)_{4-a}$ (R is substitution or an unsubstituted hydrocarbon group of the carbon numbers 1-20 independently among a formula, respectively.) a is 0, 1, 2, or 3. A silicon compound shown may be added. Although limitation is not carried out, as said silicon compound Phenyltrimethoxysilane, Phenylmethyldimethoxysilane, phenyldimethylmethoxysilane, Since the effect that what is an aryl group of the carbon numbers 6-20 accelerates a hardening reaction of a constituent is large, R in general formulas, such as diphenyldimethoxysilane, diphenyl diethoxysilane, and triphenylmethoxysilane, is preferred. Especially diphenyldimethoxysilane and diphenyl diethoxysilane are low cost, and especially since they are easy to receive, they are preferred. As for loadings of this silicon compound, about 0.01-20 weight sections are preferred to (A) ingredient 100 weight section, and its 0.1 - 10 weight section is still more preferred. If loadings of a silicon compound are less than this range, an effect of accelerating a hardening reaction may become small. On the other hand, when loadings of a silicon compound exceed this range, hardness and tensile strength of a hardened material may fall.

[0269]

A physical-properties regulator which adjusts the tractive characteristics of a hardened material generated if needed to a hardenability constituent of this invention may be added. Although not limited especially as a physical-properties regulator, for example Methyl trimetoxysilane, Alkyl alkoxysilane, such as dimethyldimethoxysilane, trimethylmethoxysilane, and n-propyltrimethoxysilane; Dimethyldi iso propenoxysilane, Alkyl iso propenoxysilane, such as methyl TORISO propenoxysilane and gamma-glycidoxy propylmethyl JIISO propenoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, gamma-glycidoxypropyltrimetoxysilane, Vinyltrimetoxysilane, vinyldimethylmethoxysilane, gamma-aminopropyl trimethoxysilane, The alkoxysilane; silicone varnishes which have functional groups, such as N-(beta-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-mercapto propyltrimethoxysilane, and gamma-mercaptopropylmethyl dimethoxysilane; polysiloxanes are mentioned. By using said physical-properties regulator, hardness when stiffening a

constituent of this invention is raised, or hardness is lowered conversely and elongation after fracture can be taken out. The above-mentioned physical-properties regulator may be used independently, and may be used together two or more sorts.

[0270]

Especially a compound that generates a compound which has a univalent silanol group in intramolecular by hydrolysis has the operation which reduces a modulus of a hardened material without worsening stickiness of the surface of a hardened material. A compound which generates especially a trimethyl silanol is preferred. A compound indicated to JP,H5-117521,A can be raised as a compound which generates a compound which has a univalent silanol group in intramolecular by hydrolysis. A compound which generates a silicon compound which is a derivative of alkyl alcohol, such as a hexanol, octanol, and decanol, and generates R_3SiOH **, such as a trimethyl silanol, by hydrolysis, Trimethylolpropane indicated to JP,H11-241029,A. A compound which generates a silicon compound which is a derivative of polyhydric alcohol whose numbers of hydroxyl groups, such as glycerin, pentaerythritol, or sorbitol, are three or more, and generates R_3SiOH **, such as a trimethyl silanol, by hydrolysis can be raised.

[0271]

A compound which generates a silicon compound which is a derivative of an oxypropylene polymer which is indicated to JP,H7-258534,A, and generates $R_3SiOH(s)$, such as a trimethyl silanol, by hydrolysis can also be raised. A polymer which has a silicon content group which can serve as a monosilanol content compound by a hydrolytic silicon content group and hydrolysis in which bridge construction furthermore indicated to JP,H6-279693,A is possible can also be used.

[0272]

A physical-properties regulator is preferably used in the range of 0.5 - 10 weight section 0.1 to 20 weight section to (A) ingredient 100 weight section.

[0273]

In a hardenability constituent of this invention, a lappet is prevented if needed, and in order to improve workability, a thixotropic grant agent (lappet inhibitor) may be added. Although not limited especially as a lappet inhibitor, metallic soap, such as polyamide wax; hydrogenation castor oil derivative; calcium stearate, aluminum stearate, and barium stearate, is mentioned, for example. These thixotropic grant agent (lappet inhibitor) may be used independently, and may be used together two or more sorts. A thixotropic grant agent is used in the range of 0.1 - 20 weight section to (A) ingredient 100 weight section.

[0274]

A compound which contains an epoxy group in one molecule in a constituent of this invention can be used. If a compound which has an epoxy group is used, the stability of a hardened material can be improved. Compounds shown in epoxidation unsaturation oil and fat, epoxidation unsaturation fatty acid ester, alicycle fellows epoxy compounds, and an epichlorohydrin derivative as a compound which has an epoxy group, those mixtures, etc. can be illustrated. Specifically, epoxidized soybean oil, epoxidation linseed oil, a di(2-ethylhexyl) 4,5-epoxy cyclohexane-1,2-JIKABOKISHI rate (E-PS), epoxy octyl stearate, epoxy butyl stearate, etc. are raised. Especially in these, E-PS is preferred. An epoxy compound is good to use it in the range of 0.5 - 50 weight section to (A) ingredient 100 weight section.

[0275]

An oxygen hardenability substance can be used for a constituent of this invention. To an oxygen hardenability substance, an unsaturated compound which can react to oxygen in the air can be illustrated, it reacts to oxygen in the air, a cured film is formed near the surface of a hardened material, and an operation of preventing adhesion of stickiness of the surface, garbage on the surface of a hardened material, and dust is carried out. Drying oil represented with tung oil, linseed oil, etc. by example of an oxygen hardenability substance, Various alkyd resins produced by denaturalizing this compound; An acrylic polymer which denaturalized with drying oil, Epoxy system resin, silicon resin; Butadiene, chloroprene, isoprene, Diene series, such as 1,3-pentadiene, a polymerization or 1,2-polybutadiene produced by making carry out copolymerization, Liquefied polymers, such as a polymer of 1,4-polybutadiene, C5 - C8 diene, NBR produced by making carry out copolymerization of these diene series and the monomers which have copolymeric, such as acrylonitrile and styrene, so that

diene series may serve as a subject, Liquefied copolymers, these various denaturation things, etc. (a mallein-ized denaturation thing, a boiled oil denaturation thing, etc.), such as SBR, are mentioned. These may be used independently and may be used together two or more sorts. Especially among these, tung oil and a liquefied diene system polymer are preferred. Concomitant use of a catalyst and a metal drier which promote an oxidation hardening reaction may heighten an effect. As these catalysts and metal driers, metal salt, such as cobalt naphthenate, lead naphthenate, a naphthenic acid zirconium, octylic acid cobalt, and an octylic acid zirconium, an amine compound, etc. are illustrated. It is at best still more preferred to use it in the range of 0.1 – 20 weight section to (A) ingredient 100 weight section, and the amount of oxygen harderability substance used is 0.5 – 10 weight section. If an improvement of stain resistance becomes less enough when said amount used will be less than 0.1 weight sections, and 20 weight sections are surpassed, a tendency for the tractive characteristics of a hardened material, etc. to be spoiled will arise. An oxygen harderability substance is good to use it, using together with a photoresist substance as indicated to JP,H3-160053,A.

[0276]

A photoresist substance can be used for a constituent of this invention. If a photoresist substance is used, a coat of a photoresist substance is formed in the hardened material surface, and stickiness of a hardened material and the weatherability of a hardened material can be improved. By operation of light, molecular structure causes a chemical change considerably for a short time, and a photoresist substance produces physical-properties change of hardening etc. Many things, such as a constituent containing an organic monomer, oligomer, resin, or them, are known by this kind of compound, and commercial arbitrary things can be adopted as it. As a typical thing, an unsaturation acrylic compound, polycinnamic acid vinyl, or azide-ized resin can be used. As an unsaturation acrylic compound, acrylic or an methacrylic system unsaturation group 1 thru/or a monomer which it has partly, It is mixtures, such as oligomer or it, and monomers, such as propylene (or butylene, ethylene) GURIKORUJI (meta) acrylate and neopentyl GURIKORUJI (meta) dimethacrylate, or with a molecular weight of 10,000 or less oligomers is illustrated. Specifically, For example, special acrylate. ARONIKKUSU M-210 (2 Functional), ARONIKKUSU M-215, ARONIKKUSU M-220, ARONIKKUSU M-233, ARONIKKUSU M-240, ARONIKKUSU M-305 of ARONIKKUSU M-245; (three organic functions), ARONIKKUSU M-309, ARONIKKUSU M-310, Although ARONIKKUSU M-315, ARONIKKUSU M-320, ARONIKKUSU M-325, (polyfunctional) ARONIKKUSU M-400, etc. can be illustrated. a compound containing especially an acrylic functional group is preferred, and a compound which averages in one molecule and contains the three or more functional groups is preferred. (Each ARONIKKUSU is a product of Toagosei chemical industry incorporated company above.)

A polycinnamic acid vinyl derivative of many besides what is a photopolymer which uses a cinnamoyl group as a sensitization group as polycinnamic acid vinyl, and esterified polyvinyl alcohol with cinnamic acid is illustrated. Azide-ized resin is known as a photopolymer which uses an azido group as a sensitization group, usually, a "photopolymer" (Showa 47(1972) —, on March 17) besides [which added a diazido compound as a sensitizing agent] a rubber sensitizing solution [and] printing society publication part issue, and the 93rd page – 106th page – 117th page – have detailed illustration — these — a sensitizer can be used, being able to mix and adding [it can be independent, or] if needed. Addition of accelerators, such as sensitizers, such as ketone and a nitro compound, and amines, may heighten an effect. A photoresist substance is good to use it in the range of 0.5 – 10 weight section preferably 0.1 to 20 weight section to (A) ingredient 100 weight section, and in 0.1 or less weight section, since there is no effect which improves weatherability, and a hardened material becomes hard too much and produces a cracking crack in 20 or more weight sections, it is not desirable.

[0277]

An antioxidant (antiaging agent) can be used for a constituent of this invention. If an antioxidant is used, the weatherability of a hardened material can be improved. Although a hindered phenol system, a mono- phenol system, a bisphenol system, and a polyphenol system can be illustrated as an antioxidant, especially a hindered phenol system is preferred. Similarly, Tinuvin 622LD, tinuvin 144;CHIMASSORB944LD, CHIMASSORB119floor-line(all are Ciba-Geigy Japan, Inc. make above);MARK LA-57, MARK LA-62, MARK LA-67, and MARK LA-63 and MARK LA-68, (All are ADEKAAGASU chemicals incorporated company make above);, A hindered amine light stabiliser

shown in SANORU LS-770, SANORU LS-765, SANORU LS-292, SANORU LS-2626, SANORU LS-1114, and SANORU LS-744 (all are the Sankyo Co., Ltd. make above) can also be used. An example of an antioxidant is indicated also to JP,H4-283259,A or JP,H9-194731,A. It is at best still more preferred to use it in the range of 0.1 – 10 weight section to (A) ingredient 100 weight section, and the amount of antioxidant used is 0.2 – 5 weight section.

[0278]

Light stabilizer can be used for a constituent of this invention. If light stabilizer is used, photooxidation degradation of a hardened material can be prevented. Although a benzotriazol system, a hindered amine system, a benzoate system compound, etc. can be illustrated as light stabilizer, especially a hindered amine system is preferred. It is at best still more preferred to use it in the range of 0.1 – 10 weight section to (A) ingredient 100 weight section, and the amount of light stabilizer used is 0.2 – 5 weight section. An example of light stabilizer is indicated also to JP,H9-194731,A.

[0279]

When an unsaturation acrylic compound is used especially as a photoresist substance in a constituent of this invention, It is preferred to use a tertiary amine content hindered amine light stabiliser as a hindered amine light stabiliser as indicated to JP,H5-70531,A because of preservation stability improvement of a constituent. As a tertiary amine content hindered amine light stabiliser. ** tinuvin 622LD and tinuvin 144; CHIMASSORB119floor line. (All are the Ciba-Geigy Japan, Inc. make above);MARKLA-57, LA-62, LA-67, LA-63 (all are ADEKAAGASU chemicals incorporated company make above); SANORU LS-765, LS-292, LS-2626, LS-1114, LS-744. (All are the Sankyo Co., Ltd. make above) etc. — light stabilizer can be illustrated.

[0280]

An ultraviolet ray absorbant can be used for a constituent of this invention. If an ultraviolet ray absorbent is used, the surface weatherability of a hardened material can be improved. Although a benzophenone series, a benzotriazol system, a salicylate series, a substitution tolyl system, a metal chelate system compound, etc. can be illustrated as an ultraviolet ray absorbent, especially a benzotriazol system is preferred. It is at best still more preferred to use it in the range of 0.1 – 10 weight section to (A) ingredient 100 weight section, and the amount of ultraviolet ray absorbent used is 0.2 – 5 weight section. It is preferred to use together and use a phenol system, a hindered phenolic antioxidant, a hindered amine light stabiliser, and a benzotriazol system ultraviolet ray absorbent.

[0281]

An ingredient which limitation in particular does not have in the method of preparation of a hardenability constituent of this invention, for example, was described above is blended, it kneads under ordinary temperature or heating using a mixer, a roll, a kneader, etc., or an ingredient is dissolved using a little suitable solvents, a usual method of mixing is adopted, and it gets. A many liquid [, such as 1 liquid type and a two-component type,] type compound can also be made and used by combining these ingredients suitably.

[0282]

If a hardenability constituent of this invention is exposed into the atmosphere, by operation of moisture, it will form network structure in three dimensions, and will harden it promptly to a solid which has rubber-like elasticity.

[0283]

It faces using a hardenability constituent of this invention, If needed Advesive improving agents other than an aminosilane, a physical-properties regulator, It is possible to add suitably various additive agents, such as a preservation stability improving agent, an ultraviolet ray absorbent, a metal deactivator, anti-ozonant, light stabilizer, amine system radical chain inhibitor, the Lynn system peroxide decomposition agent, lubricant, paints, and a foaming agent.

[0284]

A hardenability constituent of this invention can be used for sealant, such as a binder, a building, a marine vessel, and a super highway, adhesives, modeling material, a vibroisolating material, a sound deadener, a sound insulating material, a charge of foam, a paint, a gunning material, etc. Electrical insulation materials, such as electric electronic component materials, such as a solar cell rear-face sealing agent, pre-insulation an electric wire, material for cables, Elastic adhesives, powder coatings, casting material, a medical-application rubber material, a medical-application binder, A sealing material for masonry joints of sheathing materials, such as a medical equipment sealant, food packing

material, and a sizing board, A coating material, a primer, a conductive material for electromagnetic wave cover, a thermally conductive material, A charge of a hot melt material, a potting agent for electric electrons, a film, a gasket, It is available for various uses, such as a fluid-sealant agent used in various molding materials and wired sheet glass and a sealing agent for rust prevention / water proof of the glass laminate and face (cut section), autoparts, electrical machinery parts, several kinds of machine part, etc. Since, or help of a primer is borrowed and it may stick to substrates of a **** large area, such as glass, porcelain, wood, metal, and a resin-molding thing, it is usable also as various seal constituents and adhesion constituents of a type. A hardenability constituent of this invention from excelling in stability, endurance, and creeping property. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions. Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels, It is desirable, especially when it is considered as the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building and uses.

[Effect of the Invention]

[0285]

The hardenability constituent of this invention is excellent in stability, endurance, and creep resistance.

[Best Mode of Carrying Out tha Invention]

[0286]

Although working example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these working example.

[0287]

(Synthetic example 1)

Use polyoxypropylene triol of the molecular weight 3,000 [about] as an initiator, and propylene oxide is polymerized in a zinc hexa cyanocobaltate glyme complex compound catalyst, Number average molecular weight about 26,000 (polystyrene reduced molecular weight in which the column measured the solvent using THF using the TOSOH TSK-GEL H type using TOSOH HLC-8120GPC as a liquid-sending system) polypropylene oxide was obtained. Then, the methanol solution of NaOMe of the equivalent was added 1.2 times to the hydroxyl group of this hydroxyl group end polypropylene oxide, and methanol was distilled off, and also the allyl chloride was added, and the hydroxyl group of the end was changed into the allyl group. Decompression devolatilization removed the unreacted allyl chloride. To allyl end polypropylene oxide 100 weight section which is not refined [which was obtained], n-hexane 300 weight section, After it carried out mixed stirring of the water 300 weight section further at the hexane solution obtained by centrifugal separation removing water after carrying out mixed stirring of the water 300 weight section and centrifugal separation removed water again, decompression devolatilization removed hexane. By the above, the end obtained 3 organic-functions polypropylene oxide of the number average molecular weight 26,000 [about] which is an allyl group.

[0288]

150 ppm of platinum content 3wt% of platinum vinyl siloxane complexes isopropanol solutions are made into a catalyst to allyl end polypropylene oxide 100 obtained weight section, It was made to react to methyl dimethoxysilane 1.4 weight section at 90 ** for 5 hours, and the methyl dimethoxy silyl group and polyoxyalkylene series polymer (A-1) was obtained. Measurement by ^{1}H-NMR (it measures in a $CDCl_3$ solvent using JEOL JNM-LA400) averaged the methyl dimethoxy silyl group of the end per molecule, and they were 2.3 pieces.

[0289]

(Working example 1-4 and comparative examples 1-2)

Organic polymer (A-1) 100 weight section which has the reactive silicon group obtained in the synthetic example 1 according to the combination formula shown in Table 1. Surface treatment colloid calcium carbonate (product made from Shiraishi Industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chamicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make.) SANORU LS770! weight section and an ultraviolet ray

absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) silicate (made in a col coat.) given in three weight sections and Table 1 Made in an ethyl silicate 28; col coat, ethyl silicate 40; Made in a col coat, a curing catalyst (the Japanese east -- transformation -- make and the dibutyltin bisacetylacetonate (trade name: U-220); Japanese east -- transformation -- make and the product made from neo decanoic acid tin (divalent) (trade name: U-50); Japan epoxy resin,) given in the amount part of methylsilicate 51 duplexs, and Table 1 Neo decanoic acid (trade name: BASA tick 10); the description to Table 1 of the Wako Pure Chemical Industries make and lauryl amine carried out number-of-copies addition, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.

[0290]

(Hauling physical properties of a hardened material)

It was 23 **x3 +50 **x recuperated in the class product of Table 1 on the 4th, and the sheet about 3 mm thick was created. [per day] It examined by having pierced this sheet to the No. 3 dumbbell type, and having pulled by a part for 200-mm/in hauling speed, and was extended at the time of intenaity (MPa) and Eb:fracture at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A result is shown in Table 1.

[0291]

(Recovery)

It was 23 **x3 +50 **x recuperated in the class product of Table 1 on the 4th, and tha sheet about 3 mm thick was created. [per day] This sheet was pierced to the No. 3 dumbbell type, and where 20 mm is pulled to 40 mm between the marked lines (100% extension), it fixed at 60 ** for 24 hours. The recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. It means that the one where the recovery is larger is excellent in stability. A result is shown in Table 1.

[0292]

(Creep measurement using the piece of a dumbbell)

It was 23 **x3 +50 **x recuperated in the class product of Table 1 on the 4th, and the sheet about 3 mm thick was created. [per day] This sheet was pierced to the No. 3 dumbbell type, and the marked line of 20 mm of intervals was described. The end of this piece of a dumbbell was fixed in 60 ** oven, and the piece of a dumbbell was hung. 0.4 time as much load as M50 value obtained by the above-mentioned tension physical-properties measurement of this hardened material was imposed on the lower end of the hung piece of a dumbbell. The displacement difference of the distance between the marked lines of 200 hours after immadietely after imposing load was measured. It means that the one where a displacemant difference is smaller is excellent in creep rasistance. A result is shown in Table 1.

[0293]

[Table 1]

組成（重量部）		実施例				比較例	
		1	2	3	4	1	2
有機重合体（A）成分	光硬化性	A—1	100	100	100	100	100
	充填材	白艶華CCR	120	120	120	120	120
		タルク—ハ—820	20	20	20	20	20
	可塑剤	DIDP	55	55	55	55	55
	チクソ性付与剤	ディスパロン #6500	2	2	2	2	2
	光安定剤	サノールLS-770	1	1	1	1	1
	紫外線吸収剤	チヌビン327	1	1	1	1	1
	酸化防止剤	ノクラックSP	1	1	1	1	1
	接着剤	A-171	2	2	2	2	2
		A-1120	3	3	3	3	3
	接着性付与剤	スチルサート28	2	2			
	シリケート（B）成分	スチルサート40			2		
		スチルサート51				2	
硬化触媒	有機スズ系触媒	スタンBL-220	2				2
		スタンBL-50		3.4	3.4	3.4	
	触媒（硬化）量			1.2	1.2	1.2	1.2
		ラウリルアミン		0.75	0.75	0.75	0.75
	混合		54	84	86	26	80
硬化物物性	復元率	(%)				30.2	2.2
	グリーン	(mm)	15.1	1.6	1.2	1.4	0.43
	M50	(MPa)	0.53	0.46	0.48	0.50	0.42
	Tb	(MPa)	2.00	2.27	2.61	2.35	1.96
	Eb	(%)	297	400	442	389	385

[0294]

As shown in the comparative example 1 of Table 1, when organic tin (U-220) is used as a curing catalyst, especially the recovery of creep resistance is low bad silicate additive-free. However, as shown in working example 1, stability and creep resistance are notably improved by addition of silicate. As shown in the comparative example 2, when organic tin (U-220) is used for ***, carboxylic acid tin salt (neo SUTAN U-50), etc. as a curing catalyst, stability and creep resistance also with good silicate additive-free are shown, but. As shown in working example 2-4, stability and creep resistance further outstanding by silicate addition were shown. The ethyl silicate 40 and the methylsilicate 51 which were used in working example 3-4 are a condensate of a tetraethoxysilane and a tetramethoxy silane, respectively, and showed the especially outstanding effect.

[0295]

(Synthetic example 2)

Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 14,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Allyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1. To this allyl end polypropylene oxide, in the same procedure as the synthetic example 1, it was made to react to trimethoxysilane and the polyoxyalkylene series polymer (A-2) which has an average of 1.5 trimethoxysilyl groups at the end was obtained.

[0296]

(Synthetic example 3)

To the allyl end polypropylene oxide obtained in the synthetic example 2, in the same procedure as the synthetic example 1, it was made to react to triethoxysilane and the polyoxyalkylene series polymer (A-3) which has an average of 1.5 triethoxy silyl groups at the end was obtained.

[0297]

(Synthetic example 4)

To the allyl end polypropylene oxide obtained in the synthetic example 2, in the same procedure as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-4) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.

[0298]

(Working example 5-11 and comparative examples 3-5)

Organic polymer (A-2-4) 100 weight section which has the reactive silicon group obtained in the synthetic examples 2-4 according to the combination formula shown in Table 2, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP12 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make,) SANORU LS7701 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals,) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make,) A-1120) Three weight sections, number of copies given [silicate (made in a col coat, methylsilicate 51)] in Table 2, the curing catalyst (Japanese east transformation make and dibutyltin bisacetylacetonate (trade name: U-220); the Sankyo Organic Chemicals make, a dibutyltin JIRAURI rate (trade name: STANN BL)) of the (D) ingredient given in Table 2, or the curing catalyst (the Japanese east --- transformation --- make,) of the (C) ingredient The desorption to Table 2 of neo decanoic acid tin (divalent) (trade name: U-50) and amine (the Wako Pure Chemical Industries make, lauryl amine) carried out number-of-copies addition, after kneading in the etate where moisture does not exist substantially under drying conditions, it sealed in the dampproof container end 1 liquid mold-curing nature constituent was obtained.

[0299]

It examined by having pulled by the same method as the above-mentioned using the class product of Table 2, and was extended at the time of intensity (MPa) and Eb:fracture at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A result is shown in Table 2.

[0300]

The recovery was measured by the same method as the above-mentioned using the class product of Table 2. However, the stretched state was fixed at 23 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. A result is shown in Table 2.

[0301]

(Creep measurement using a shear sample)

The displacement difference with the 140-hour back immediately after creating the ** sample which is not carried en area of 20 mm x 25 mm and 1 mm in thickness using the class product of Table 2, imposing 0.1MPa load for what recuperated [23 **x3 +50 **x] itself on the 4th in 60 ** oven, and imposing load was measured. [per day] The displacement difference made O x for the thing below

0.4 mm, and the displacement difference carried out a thing of 0.4 mm or more. A result is shown in Table 2.

[0302]

[Table 2]

組成（重量部）		反応性ケイ素基の導入	実施例						比較例			
			5	6	7	8	9	10	11	3	4	5
有機重合体（A1）成分	A-2	ﾒﾁﾙｼﾘﾙ化	100	100								
	A-3	ﾒﾁﾙｼﾘﾙ化			100	100	100	100	100	100	100	100
	A-4	ﾒﾁﾙｼﾞﾒﾄｷｼｼﾘﾙ化										
充填材	白艶華CCR		120	120	120	120	120	120	120	120	120	120
	ﾎﾜｲﾄﾝ-SB-820		20	20	20	20	20	20	20	20	20	20
可塑剤	DIDP		12	12	12	12	12	12	12	12	12	12
チクソ性付与剤	ﾃﾞｨｽﾊﾟﾛﾝ 6500		2	2	2	2	2	2	2	2	2	2
光安定剤	ﾁﾊﾞｽﾋﾞﾝ 770		1	1	1	1	1	1	1	1	1	1
紫外線吸収剤	ﾁﾊﾞｽﾋﾞﾝ 327		1	1	1	1	1	1	1	1	1	1
酸化防止剤	ﾉｸﾗｲﾄ 300											
	A-171		2	2	2	2	2	2	2	2	2	2
接着性付与剤	A-1120		3	3	3	3	3	3	3	3	3	3
シラノール（B）成分	ｼﾗﾉｰﾙ-351							2				
（D）成分	ｽﾀﾝﾎﾞｰﾙ-220		0.2		0.2		2			0.2	2	
硬化触媒	Stann BL			0.3								3
（C）成分	ｽﾀﾝﾎﾞｰﾙ-50									3.4		
アミン	(%)		93	93	93	93	94	96	96	0.75	67	47	64
硬化性			○	○	○	○	○	○	○	○	×	×	×
クリープ（その他）		(MPa)	0.94	0.95	1.13	0.92	0.92	1.15	0.94	1.01	0.85	0.82
硬化物物性	M-5	(MPa)	2.24	2.20	2.61	2.35	2.08	2.20	2.18	2.83	2.84	2.70
	E b	(%)	193	196	184	205	208	167	216	269	340	370

[0303]

When the reactive silicon group of an end uses the organic polymer (A-2-3) which is the Tori alkoxy silyl groups from comparison with working example 5-9 of Tabla 2, and the comparative examples 3-5, stability and creep resistance are improved notably. Working example 10 which added silicate, and working example 11 using carboxylic acid tin salt (neo SUTAN U-50) as a curing catalyst showed the further outstanding recovery.

[0304]

(Synthetic example 5)

To the allyl end polypropylene oxide obtained in the synthetic example 1, in the same procedure as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-5) which has an average of two methyl dimethoxy silyl groups at the end was obtained.

[0305]

(Synthetic example 6)

Use polyoxypropylene triol of the molecular weight 3,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 26,000 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Metallyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1 except making an allyl chloride into chloridation metallyl. 0.5 copy of platinum content 3wt% of platinum vinyl siloxane complexes isopropanol solution is made into a catalyst to this metallyl end polypropylene oxide 100 weight section, oxygen — 6vol% — mixed sulfur at a rate of 1 eq/Pt1eq under the atmosphere of the nitrogen to contain, it was made to react to methyl dimethoxysilane 3.2 weight section at 90 ** for 5 hours, and the polyoxyalkylene series polymer (A-6) which has an average of 2.8 methyl dimethoxy silyl groups at the end was obtained.

[0306]

(Working example 12-14 and comparative example 6)

Organic polymer (A-1, A-4-6) 100 weight section which has the reactive silicon group obtained in the synthetic example 1 and the synthetic examples 4-6 according to the combination formula shown in Table 3, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make,) SANORU LS7701 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, As the amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (Nippon Unicar make, A-1120) 3 weight section, and a curing catalyst, Carboxylic acid tin salt (Japanese east transformation make, neo decanoic acid tin (divalent) (trade name: U-50)) 3.4 weight section, Carboxylic acid (product made from Japan epoxy resin, neo decanoic acid (trade name: BASA tick 10)) 1.2 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section are added, After kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.

[0307]

It examined by having pulled by the same method as the above-mentioned using the class product of Table 3, and was extended at the time of intensity (MPa) and Eb:fracture at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A result is shown in Table 3.

[0308]

The recovery was measured by the same method as the above-mentioned using the class product of Table 3. However, the stretched state was fixed at 60 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. A result is shown in Table 3.

[0309]

The displacement difference of the distance between the marked lines of 200 hours after immediately

after performing creep measurement using the piece of a dumbbell, and imposing load by the same method as the method of working example 1-4, using the class product of Table 3, was measured. A result is shown in Table 3.

[0310]

[Table 3]

組成（重量部）			実施例 12	13	14	比較例 6
		1分子あたりの反応性ケイ素基				
有機重合体（A-2）成分	A－5	2.0個	100			
	A－1	2.4個		100		
	A－6	2.8個			100	
	A－4	1.5個				100
充填材	白艶華CCR		120	120	120	120
	ﾀｲｶ-R-820		20	20	20	20
	DIDP		55	55	55	55
可塑剤	ﾃﾞｽﾊﾟﾛﾝ #6500		2	2	2	2
チクソ性付与剤	ｻﾝｿﾙﾊﾞ-770		1	1	1	1
光安定剤	ﾁﾇﾋﾞﾝ327		1	1	1	1
紫外線吸収剤	ﾊﾟﾗｼｽSP		1	1	1	1
酸化防止剤	A-171		2	2	2	2
脱水剤	A-1120		3	3	3	3
接着性付与剤	ｻﾝｽﾋﾞｭｱ50		3.4	3.4	3.4	3.4
硬化触媒	加水ｼﾞﾌﾞﾁﾝ		1.2	1.2	1.2	1.2
	ﾈｵｽﾀﾝU210		0.75	0.75	0.75	0.75
	ﾃﾉﾘﾙﾀﾝ		78	81	86	73
増ｸﾚｰﾌﾞ		(%)	2.5	2.2	1.3	3.2
硬化物物性	M50	(MPa)	0.35	0.43	0.68	0.38
	Tb	(MPa)	2.39	2.30	1.87	2.02
	Eb	(%)	601	483	273	502

[0311]

Comparison with working example 12-14 of Table 3 and the comparative example 6 shows that the organic polymer with many reactive silicon groups per molecule (A-1, A-5-6) is excellent in stability and creep resistance.

[0312]

(Synthetic example 7)

Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl

group end polypropylene oxide of the number average molecular weight 28,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Metallyl end polypropylene oxide was obtained in the same procedure as the synthetic example 6. To this metallyl end polypropylene oxide, in the same procedure as the synthetic example 6, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-7) which has an average of 1.9 methyl dimethoxy silyl groups at the end was obtained.

[0313]

(Synthetic example 8)

To the metallyl end polypropylene oxide obtained in the synthetic example 7, in the same procedure as the synthetic example 6, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-8) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.

[0314]

(Synthetic example 9)

Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 28,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Allyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1. To this allyl end polypropylene oxida, in the same procedura as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-9) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.

[0315]

(Working example 15-16 and comparative examples 7-8)

Organic polymer (A-4, A-7-9) 100 weight section which has the reactive silicon group obtained in the synthetic example 4 and the synthetic examples 7-9 according to the combination formula shown in Table 4, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make,) SANORU LS7701 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals,) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethy)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) Three weight sections and the amount part of curing catalyst dibutyltin bisacatylacetonate (Japaneae sast transformation make, neo SUTAN U-220) duplexs ware added, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-couring nature constituent was obtained.

[0316]

It examined by having pulled by the same method as the above-mentioned using the class product of Table 4, and was extended at the time of intensity (MPa) and Eb:fracture at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A result is shown in Table 4.

[0317]

The recovery was measured by the same method as the above-mentioned using the class product of Table 4. However, the stretched state was fixed at 23 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 24 hours afterward. A result is shown in Table 4.

[0318]

The displacement difference of the distance between the marked lines of 45 hours after immediately after performing creep measurement using the piece of a dumbbell, and imposing load by the same method as the method of working example 1-4, using the class product of Table 4, was measured. A result is shown in Table 4.

[0319]

[Table 4]

組成（重量部）			反応性ケイ素基導入前の末端基の構造	1分子あたりの反応性ケイ素基	実施例		比較例
					15	16	7	8
有機重合体	（A3）成分	A－7	メトキシ基	1.8個	100			
		A－8	メトキシ基	1.8個		100		
		A－9	メトキシ基	1.5個			100	
		A－4	メトキシ基	1.5個				100
充填材			白艶華CCR		120	120	120	120
			ﾊｲﾌﾞﾘｯﾄﾞ-820		20	20	20	20
			DIDP		55	55	55	55
可塑剤			ﾓﾉｼﾞｸﾙ #6500		2	2	2	2
チクソ性付与剤			ｻｰﾓｽﾋﾞｽﾀ-770		1	1	1	1
光安定剤			ﾁﾊﾞｿﾌﾞ327		1	1	1	1
紫外線吸収剤			ﾊﾞﾅｰｽﾞBP		1	1	1	1
酸化防止剤			A-171		2	2	2	2
脱水剤			A-1120		3	3	3	3
接着性付与剤			ｽﾀｽﾘﾙ-220		2	2	2	2
硬化触媒					86	84	74	75
指触乾燥				(hr)	15	22	44	41
クリープ				(MPa)	0.41	0.21	0.19	0.39
硬化物物性		M50		(MPa)	2.71	3.02	2.60	1.90
		Tb		(%)	852	1019	1018	403
		Eb						

[0320]
Comparison with working example 15-16 of Table 4 and the comparative examples 7-8 showa that the organic polymer (A-7-8) which introduced the reactive silicon group to the metallyl group end

organicity polymer is excellent in stability and creep resistance.
[0321]
(Synthetic example 10)
To the allyl end polypropylene oxide obtained in the synthetic example 1, in the same procedure as the synthetic example 1, it was made to react to triethoxysilane and the polyoxyalkylene series polymer (A-10) which has an average of 2.3 triethoxy silyl groups at the end was obtained.
[0322]
(Working example 9-10 and comparative examples 9-10)
Organic polymer (A-1, A-10) 100 weight section which has the reactive silicon group obtained in the synthetic example 1 and the synthetic example 10 according to the combination formula shown in Table 5, Surface treatment colloid calcium carbonate (product made from Solvay, Winnofil SPM) 120 weight section, Titanium oxide (product made from Kerr-McGee, RFK-2) 20 weight section, DIUP50 weight section, Thixotropic grant agent (product made from Cray Valley, Crayvallasosuper) 5 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, As a dehydrator, the amount part of vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, gamma-aminopropyl triethoxysilane (the Nippon Unicar make.) which is the (G) ingredient as an adhesion grant agent A-1100) Or add N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (Nippon Unicar make, A-1120) 3 weight section and the amount part of curing catalyst dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs, After kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.
[0323]
The recovery was measured by the same method as the above-mentioned using the class product of Table 5, However, the stretched state was fixed at 60 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. A result is shown in Table 5.
[0324]
The displacement difference of the distance between the marked lines of 140 hours after immediately after performing creep measurement using a shear sample and imposing load by the same method as the method of working example 5-11, using the class product of Table 5, was measured. As for the valuation basis, the displacement difference made O x for the thing below 0.4 mm, and the displacement difference carried out a thing of 0.4 mm or more. A result is shown in Table 5.
[0325]
(Hardenability of a hardenability constituent)
The class product of Table 5 was thinly lengthened in thickness of about 3 mm, and time (leather-covered time) until the surface stretches a hide under 23 ** and 50% of humidity RH conditions was measured. The one where leather-covered time is shorter means that hardenability is excellent. A result is shown in Table 5.
[0326]
[Table 5]

組成（重量部）		反応性ケイ素基の構造	実施例 17	比較例 9	比較例 10
有機重合体	（A4）成分	A－10	MDHキシリル基	100	100	
		A－1	メチルジメトキシシリル基			100
充填材		Winnofil SPM		120	120	120
		RFK-2		20	20	20
可塑剤		DIUP		50	50	50
チクソ性付与剤		Crayvallac super		5	5	5
光安定剤		サノールLS-770		1	1	1
紫外線吸収剤		チヌビン327		1	1	1
酸化防止剤		ノクラックSP		1	1	1
脱水剤		A-171		2	2	2
接着性付与剤	（G）成分	A-1100	MDHキシリル基	3		3
		A-1120	MDHキシリル基		3	2
硬化触媒		オクチル酸Sn-220		2	2	2
復元率		(%)		87	85	25
クリープ（せん断）				○	○	×
皮張時間	貯蔵前		(min)	20	15	15
	貯蔵後		(min)	20	5	15

[0327]
If the aminosilane which has a triethoxy silyl group which is the (G) ingredient as an adhesive grant agent is combined with the end of the (A4) ingredient using the polymer which has a triethoxy silyl group as an organic polymer as shown in working example 17 of Table 5, Excelling in stability and creep resistance, change of the skinning time in storage order is small, and storage stability is good.

[0328]
(Working example 18 and comparative examples 11-12)
Organic polymer (A-2) 100 weight section which has the reactive silicon group obtained in the synthetic example 2 according to the combination formula shown in Table 6, as DIDP30 weight section and a dehydrator — triethoxysilane (made in a col coat.) the N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) which is the (H) ingredient as the amount part of ethyl silicate 28 duplexs, and an adhesion grant agent A-1120) or N-beta-(aminoethyl)-gamma-aminopropyl triethoxysilane (the Shin-Etsu Chemical make.) It added, KBE-6033 weight section and the amount part of curing catalyst dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs were sealed in the glassware which carried out the nitrogen purge, and 1 liquid mold-curing nature constituent was obtained. In the comparative example 11, the leather-covered time test was performed under 50% of 23 ** humidity RH conditions, without recuperating oneself in this 1 liquid mold-curing nature constituent. In working example 18 and the comparative example 12, after promoting the ester exchange reaction between reactive silicon groups by recuperating oneself for seven days at 50 ** in these 1 liquid mold-curing nature constituents, the leather-covered time test was performed under 50% of 23 ** humidity RH conditions. A result is shown in Table 6.
[0329]
[Table 6]

組成（重量部）		反応性ケイ素基の構造	実施例 18	比較例 11	12
有機重合体	（A4）成分	A－2	100	100	100
可塑剤		DIDP	30	30	30
脱水剤		エチルシリケート28	2	2	2
接着性付与剤	（H）成分	A-1120	3	3	
		KBE-603			3
硬化触媒		ネオスタンU-220	2	2	2
皮張時間	50℃×7日の養生		有	無	有
		(min)	3	13	12

[0330]
As shown in working example 18 of Table 6, the polymer which has a triethoxy silyl group is used for the end of the (A4) ingredient as an organic polymer, If the aminosilene which has a methoxy silyl

group which is the (H) ingredient as an adhesive grant agent is combined and an ester exchange reaction is promoted by care of health, the hardenability of an organic polymer can be raised notably.
[0331]
(Working example 19-20 and comparative example 13)
Organic polymer (A-10) 100 weight section which has the reactive silicon group obtained in the synthetic example 10, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make.) SANORU LS770I weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicels.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) Three weight sections and the various below-mentioned curing catalysts were added, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dempproof container and 1 liquid mold-curing nature constituent was obtained. the neo decanoic acid (the product made from Japan epoxy resin.) which is a non-tin catalyst of the (E) ingredient as a curing catalyst what carried out concomitant use addition of BASA tick 106 weight section and the amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section — working example 19 and isopropoxy titanium bis (ethylacetoacetate) (the Matsumoto Trading make.) What carried out Olga Chicks TC-750 8.5 weight-section addition was made into working example 20. What carried out the amount part addition of dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs was made into the comparative example 13.
[0332]
As a result of measuring the recovery by the same method as the above-mentioned using these class products, the hardened materiel of working example 19 and working example 20 showed the recovery higher than the hardened material of the comparative example 13.
[0333]
(Synthetic example 11)
Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 25,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Allyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1. To this allyl end polypropylene oxide, in the same procedure as the synthetic example 1, it was made to react to triethoxysilane and the polyoxyalkylene series polymer (A-11) which has an average of 1.5 triethoxy silyl groups at the end was obtained.
[0334]
(Synthetic example 12)
To the allyl end polypropylane oxide obtained in the synthetic example 11, in the same procedure as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-12) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.
[0335]
(Working example 21 and comparative examples 14-15)
Organic polymer (A-11, A-12) 95 weight section which has the reactive silicon group obtained in the synthetic example 11 and the synthetic example 12, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Toagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicels], tinuvin 327) 1 weight section, Zero copy of minute hollow body (the product made from

the Fuji SHIRISHIA chemicals, the FUJIBA lune H-40) which is antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section and the (F) ingredient, or 20 copies were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin. What added 20 copies of minute hollow bodies was made into working example 21, using (A-12) as an organic polymer. What added zero copy of minute hollow body was made into the comparative example 14, using (A-12) as an organic polymer, and what added 20 copies of minute hollow bodies was made into the comparative example 15, using (A-11) as an organic polymer.

[0336]

Using the mixture of 2-ethylhexanoic acid tin (Japanese east transformation make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section as a hardening agent, above-mentioned base resin and hardening agent were mixed uniformly, and workability (********) and endurance were evaluated.

[0337]

The constituent of working example 21 had workability better than the comparative example 14, and its endurance was better than the comparative example 15.

[0338]

(Working example 22 and comparative example 16)

Organic polymer (A-1) 95 weight section which has the reactive silicon group obtained in organic polymer (A-10) 70 weight section which has the reactive silicon group obtained in the synthetic example 10, or the synthetic example 1, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Teagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section and antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin. What added 70 copies of (A-10) as an organic polymer was made into working example 22, and what added 95 copies of (A-1) as an organic polymer was made into the comparative example 16. As a hardening agent, to this base resin, the mixture of 2-ethylhexanoic acid tin (Japanese east transformation make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section was added, and the recovery was measured to it.

[0339]

The constituent of working example 22 showed the recovery higher than the comparative example 16, stopping weight % of an organic polymer low.

[0340]

(Working example 23 and comparative example 17)

Organic polymer (A-10) 95 weight section which has the reactive silicon group obtained in the synthetic example 10, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Teagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section, Antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section and zero copy of epoxy resin (the product made from Japan epoxy resin, Epicoat 828), or five copies were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin. What added five copies of epoxy resins was made into working example 23. What added zero copy of epoxy resin was made into the comparative example 17. As a hardening agent, to this base resin, the mixture of 2-ethylhexanoic acid tin (Japanese east transformation

make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section was added, and the recovery was measured to it.

[0341]

The constituent of working example 23 showed the recovery higher than the comparative example 17.

[0342]

(Working example 24 and comparative example 18)

Organic polymer (A-10) 95 weight section which has the reactive silicon group obtained in the synthetic example 10, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Teagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section and antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin.

[0343]

2-ethylhexanoic acid tin (Japanese east transformation make, U-28) (divalent) 3 weight section and amine (the Wako Pure Chemical Industries make,) lauryl amine 0.75 weight section and dibutyltin bisacetylacetonate (the Japanese east -- transformation -- make.) The thing using the mixture of neo SUTAN U-220 0.1 weight section as a hardening agent is made into working example 24, The thing using the mixture of 2-ethylhexanoic acid tin (Japanese east transformation make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section as a hardening agent was made into the comparative example 18. Base resin and a hardening agent were mixed uniformly and the recovery and thin layer hardenability were evaluated.

[0344]

The constituent of working example 24 showed good thin layer hardenability rather than the comparative example 18, while the high recovery was shown.

[0345]

(Synthetic example 13)

To the allyl end polyisobutylene obtained according to the example of manufacture of JP,H11-209839,A, under existence of Pt catalyst, it was made to react to triethoxysilane and the polyisobutylene (A-13) which has a triethoxy allyl group at the end was obtained.

[0346]

(Synthetic example 14)

To the allyl and polyisobutylene obtained in the synthetic example 13, under existence of Pt catalyst, it was made to react to methyl dimethoxysilane and the polyisobutylene (A-14) which has a methyl dimethoxy silyl group at the end was obtained.

[0347]

(Working example 25 and comparative example 19)

To organic polymer (A-13, A-14) 100 weight section which has the reactive silicon group obtained in the synthetic example 13 and the synthetic example 14, the amount part of dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs was added, and the hardened material was obtained. The thing using (A-13) as an organic polymer was made into working example 25, and the thing using (A-14) was made into the comparative example 19. The hardened material of working example 25 showed the recovery higher than the comparative example 19.

[0348]

(Synthetic example 15)

CuBr (4.2g) and acetonitrile (27.3g) were added to the reaction vessel with an agitator, and it stirred for 15 minutes at 65 ** under a nitrogen atmosphere. Acrylic acid n-butyl (100g), 2, 5-dibromo diethyl adipate (8.8g), and acetonitrile (16.6g) were added to this, and stirring mixing was improved.

Pentamethyl diethylenetriamine (0.17g) was added and the polymerization was made to start. Acrylic acid n-butyl (400g) was dropped continuously, heating and stirring at 70 **. Dividing addition of the triamine (0.68g) was carried out in the middle of dropping of acrylic acid n-butyl.
[0349]
When monomer conversion reachas to 96%, after devolatilizing a ** monomer and acetonitrile at 80 **, 1,7-octadien (53.7g), acetonitrile (132g), and triamine (1.69g) were added. It heated and stirred at 70 ** succeedingly, and the mixture containing the polymer which has an alkenyl group was obtained.
[0350]
Heating devolatilization of acetonitrile in a mixture and the unreacted 1,7-octadien was carried out, and it diluted with the methylcyclohexane. The insoluble polymerization catalyst was made to sediment with a centrifuge, and was removed. Six copies (three copies of KYO word 500SH / 3 copies of KYO word 700SL [:] product [Both] made from Harmony Chemicals) of adsorbent was added to the methylcyclohexane solution of the polymer to 100 copies of polymers, and it heated and stirred under oxygen and nitrogen mixed gas atmosphere. Insoluble matter was removed and the polymer (polymer [P1]) which has an alkenyl group by condensing a polymer solution was obtained.
[0351]
After having carried out heating devolatilization (10 or less torr of decompression degrees), diluting 100 copies of the polymer with 400 copies of methylcyclohexanes further and removing solid content, stirring the obtained polymer [P1] at 180 ** for 12 hours, the solution was condensed and the polymer [P2] was obtained. The number average molecular weight of this polymer [P2] was 24800, and molecular weight distribution was 1.36. The number of the alkenyl groups introduced per one molecule of polymers was 1.8.
[0352]
To this polymer [P2], methyl orthoformate (it is 1 mol equivalent to an alkenyl group), A platinum catalyst (it is 10 mg to 1 kg of polymers as an amount of platinum metal), 1-(2-trimethoxysilyl ethynyl)-1, 1 and 3, and 3-tetramethyl disiloxane (they are 1.5 mol equivalents to an alkenyl group) were added in order, and it mixed, and heated and stirred at 100 ** under a nitrogen atmosphere for 0.5 hour. It checked by ^{1}H-NMR that the alkenyl group had disappeared by a reaction, and the trimethoxysilyl group content polymer (A-15) which condenses a reaction mixture and is made into the purpose was obtained. The number average molecular weight was 27900 and molecular weight distribution was 1.32. The number of the silyl groups introduced per one molecule of polymers was 1.7.
[0353]
(Synthetic example 16)
As opposed to the polymer [P2] obtained in the synthetic example 15, The triethoxy silyl group content polymer (A-16) was obtained like the synthetic example 15 except having used triethoxysilane (they are 3 mol equivalents to an alkenyl group) instead of 1-(2-trimethoxysilyl ethynyl)-1 used in the synthatic example 15, 1 and 3, and 3-tatramethyl disiloxane. The number average molecular weight was 28600 and molecular weight distribution was 1.48. The number of the silyl groups introduced per one molecule of polymers was 1.5.
[0354]
(Synthetic example 17)
As opposed to the polymer [P2] obtained in the synthetic example 15, It is methyl dimethoxysilane (to an alkenyl group,) instead of 1-(2-trimethoxysilyl ethynyl)-1 used in the synthetic example 15, 1 and 3, and 3-tetramethyl disiloxane. The methyl dimethoxy silyl group content polymer (A-17) was obtained like the synthetic example 15 except having used three mol equivalents. The number average molecular weight was 28400 and molecular weight distribution was 1.51. The number of the silyl groups introduced per one molecule of polymers was 1.5.
[0355]
(Working example 26-28 and comparative example 20)
as opposed to organic polymer 100 weight section which has a reactive silicon group — surface treatment colloid calcium carbonate (the product made from the Shiraishi industry,) Hakuenka CCR150 weight section and heavy calcium carbonate (the Maruo Calcium make.) 25ANANOKKUSU 20 weight section, titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 10 weight section, DIDP60 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals],

DISUPARON 6500) duplexs, light stabilizar (Sankyo make, SANORULS765) 1 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) tinuvin 2131 weight section and dehydrator vinyltrimetoxysilane (the Nippon Unicar make.) A-171) tha amount part of duplexs, and adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimathoxysilane (the Nippon Unicar make.) A-1120) Dibutyltin bisacetylacetonate (Japanese cast transformation make, neo SUTAN U-220) 0.2 weight aection was added as the amount part of duplexs, and a curing catalyst, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof containor and 1 liquid mold-curing nature constituent was obtained. The **** thing for 100 weight sections is made into working example 26 for the acrylic ester system polymer (A-15) which has the trimethoxysilyl group obtained in the synthetic example 15 as an organic polymer which has a reactive silicon group, (A-15) Make the **** thing for a total of 100 weight sections into working example 27 for the mixture of 50 weight sections and polyoxyalkylene series polymer (A-4) 50 weight section which has the methyl dimethoxy silyl group obtained in the synthetic example 4, The **** thing for 100 weight sections is made into working example 28 for the acrylic ester system polymer (A-16) which has the triethoxy silyl group obtained in the synthetic example 16, The **** thing for 100 weight sections was made into the comparative example 20 for the acrylic ester system polymer (A-17) which has the methyl dimethoxy silyl group obtained in the synthetic example 17. The hardened material of working example 26-28 showed the recovery higher than the comparative example 20.
[Industrial applicability]
[0356]
The hardenability constituent of this invention is excellent in stability, endurance, and creep resistance.

[Translation done.]

WRITTEN AMENDMENT

[Written Amendment]
[Filing date]Heisei 18(2006) October 4 (2006.10.4)
[Amendment 1]
[Document to be Amended]Claims
[Item(s) to be Amended]Whole sentence
[Method of Amendment]Change
[The contents of amendment]
[Claim(s)]
[Claim 1]
It has a silicon containing functional group which can construct a bridge by forming on silicon a siloxane bond which has three or more hydrolytic bases, an organic polymer (A1) which is at least one sort as which a principal chain skeleton is chosen from an acrylic ester system copolymer obtained by polyoxyalkylene series polymer, saturated hydrocarbon system polymer, and a living-radical-polymerization method (meta-) — and
A silanol condensation catalyst which is at least one sort chosen from carboxylic acid tin salt (C), an organic tin catalyst (D), and a non-tin catalyst (E)
A containing hardenability constituent.
[Claim 2]
A silicon containing functional group which can construct a bridge by forming a siloxane bond is a general formula (6). :

$-Si(OR^4)_3$ (6)

The hardenability constituent according to claim 1 characterized by what is expressed with (the inside of a formula and three R^4 are the organic groups of monovalence of the carbon numbers 2-20 independently, respectively).
[Claim 3]
The hardenability constituent according to claim 1 or 2, wherein a silicon containing funotional group which can construct a bridge by forming a siloxane bond is a triethoxy silyl group.
[Claim 4]
An organic polymer in which an organic polymer (A1) introduced an unsaturation group into an end, and a general formula (2) :

$H-SiX_a$ (2)

(X show a hydroxyl group or a hydrolytic basis among a formula, and three X may be the same and may differ.) — a hardenability constituent given in any 1 paragraph of Claims 1-3 being the organic polymers obtained by an addition reaction with a hydrosilane compound expressed.
[Claim 5]
An organic polymer in which an organic polymer (A1) introduced an unsaturation group into an end, and a general formula (9) :

$H-Si(OR^4)_3$ (9)

A hardenability constituent given in any 1 paragraph of Claims 1-4 being the organic polymers obtained by an addition reaction with a hydrosilane compound expressed with (the inside of a formula and three R^4 are the organic groups of monovalence of the carbon numbers 2-20 independently.

respectively).
[Claim 6]
A hardenability constituent given in any 1 paragraph of Claims 1-5 to which an organic polymer (A1) is characterized by being an organic polymer which does not contain an amide segment (-NH-CO-) substantially in a principal chain skeleton.
[Claim 7]
A hardenability constituent given in any 1 paragraph of Claims 1-6 which a silanol condensation catalyst is carboxylic acid tin salt (C), and are characterized by containing an amine compound further.
[Claim 8]
The hardenability constituent containing an organic tin catalyst (D) according to claim 7.
[Claim 9]
An organic tin catalyst (D) Dialkyl tin carboxylate, dialkyl tin oxide, $Q_eSn(OZ)_{4-e}$ and $[Q_2Sn(OZ)]_2O$

(Z expresses among a formula an organic group which has a functional group with which Q can form a coordinate bond in an inside of a hydrocarbon group of monovalence of the carbon numbers 1-20, or self for a hydrocarbon group of monovalence of the carbon numbers 1-20 to Sn.) g is 0, 1, 2, or 3. Claims 1-6 being at least one sort chosen from a group which consists of a compound shown, and a hardenability constituent given in any 1 paragraph of 8.
[Claim 10]
A hardenability constituent given in any 1 paragraph of Claims 1-8 to which carboxylic acid tin salt (C) is characterized by a carbon atom which adjoins a carbonyl group being the carboxylic acid tin salt (C1) which is the 4th class carbon.
[Claim 11]
A hardenability constituent given in any 1 paragraph of Claims 1-6 which said non-tin catalyst (E) is carboxylic acid, and are characterized by containing amine further.
[Claim 12]
The hardenability constituent according to claim 11, wherein a carbon atom in which carboxylic acid adjoins a carbonyl group is carboxylic acid which is the 4th class carbon.
[Claim 13]
A hardenability constituent given in any 1 paragraph of Claims 1-12 containing a minute hollow body (F).
[Claim 14]
A hardenability constituent given in any 1 paragraph of Claims 1-12, wherein an organic polymer (A1) is 5 to 28 % of the weight in a total amount of a hardenability constituent.
[Claim 15]
A hardenability constituent given in any 1 paragraph of Claims 2-12 containing epoxy resin (I).
[Claim 16]
A hardenability constituent given in any 1 paragraph of Claims 1-12 containing silicate (B).
[Claim 17]
The hardenability constituent according to claim 16, wherein silicate is a condensate of tetra alkoxysilane.
[Claim 18]
A general formula (7) :

$-SiR^5_c(OR^6)_{3-c}$ (7)

(Among a formula, c R^5 is the organic groups of monovalence of the carbon numbers 1-20 independently, and 3-c R^6, respectively) It is an organic group of monovalence of the carbon numbers 2-20 independently, and c shows 0, 1, or 2, respectively. A hardenability constituent given in any 1 paragraph of Claims 2-12 containing an aminosilane coupling agent (G) which has a basis expressed.
[Claim 19]
The hardenability constituent according to claim 18, wherein a basis expressed with the above-mentioned general formula (7) is a triethoxy silyl group.
[Claim 20]
A general formula (8) :

$-Si(OR^4)_3$ (6)

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond expressed with (the inside of a formula and three R^4 are the organic groups of monovalence of the carbon numbers 2-20 independently, respectively), and a general formula (8) :

$-SiR^7_d(OCH_2)_e(OR^8)_{3-d-e}$ (8)

(d R^7 is the organic groups of monovalence of the carbon numbers 1-20 independently among a formula, respectively, R^8 of a 3-d-e individual is an organic group of monovalence of the carbon numbers 2-20 independently, and d shows 0, 1, or 2 and, as for e, it shows 1, 2, or 3, respectively.) However, 3-d-e>=0 shall be satisfied. A hardenability constituent given in any 1 paragraph of Claims 2-12 which are the hardenability constituents containing an aminosilane coupling agent (H) which has a basis expressed, and are characterized by recuperating oneself beforehand in this hardenability constituent.

[Claim 21]

A general formula (6) :

$-Si(OR^4)_3$ (6)

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond expressed with (the inside of a formula and three R^4 are the organic groups of monovalence of the carbon numbers 2-20 independently, respectively), A general formula (10) obtained by carrying out the ester exchange reaction of the compound (J) which has at least one methoxy group which can carry out an ester exchange reaction to an R^4O-basis of a general formula (6) :

$-Si(OCH_3)_f(OR^4)_{3-f}$ (10)

(among a formula, 3-f R^4 is the organic groups of monovalence of the carbon numbers 2-20 independently, respectively, and f shows 1, 2, or 3.) — a manufacturing method of an organic polymer having a silicon containing functional group which can construct a bridge by forming a siloxane bond expressed.

[Claim 22]

an organic polymer obtained with a manufacturing method of Claim 21 — and

A silanol condensation catalyst which is at least one sort chosen from carboxylic acid tin salt (C), an organic tin catalyst (D), and a non-tin catalyst (E)

A containing hardenability constituent.

[Claim 23]

An object for interior panels containing Claims 1-20 and a hardenability constituent given in any 1 paragraph of 22, an object for face panels, or adhesives for car panels.

[Claim 24]

A sealing material for working joint containing Claims 1-20 and a hardenability constituent given in any 1 paragraph of 22 of a building.

[Amendment 2]

[Document to be Amended]Description

[Item(s) to be Amended]Whole sentence

[Method of Amendment]Change

[The contents of amendment]

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the hardenability constituent containing the organic polymer which has a silicon containing functional group (henceforth a reactive silicon group) which can construct a bridge by forming a siloxane bond.

[Background of the Invention]

[0002]

It is known that the organic polymer which contains at least one reactive silicon group in a molecule has the interesting character in which construct a bridge by formation of the siloxane bond

accompanied by the hydrolysis reaction of a reactive silicon group, etc., and a rubber-like hardened material is obtained with hygroscopic surface moisture etc. also in a room temperature.

[0003]

In the polymer which has these reactive silicon groups, a polyoxyalkylene series polymer and a polyisobutylene system polymer are already produced industrially, and are widely used for uses, such as a sealing material, adhesives, and a paint.

[0004]

The adhesives for interior panels, the adhesives for face panels, the adhesives for tiling, the adhesives for stone tensions, When the resin for adhesives used for the adhesives for finishing of wall, the adhesives for car panels, etc. is inferior to stability or creep resistance, an adhesives layer may pass with prudence and the stress from the outside of adherend, it may change by the time, and a panel tile, a stone, etc. may shift. Also in ceiling finishing adhesives or floor finishing adhesives, if inferior to stability or creep resistance, an adhesives layer may pass and it may change by the time, and unevenness of a ceiling surface or a floor line may arise. If the stability of the electrical and electronic equipment, an electron, and the adhesives for precision-mechanical-equipment assemblies and creep resistance are bad, an adhesives layer may pass, and it may change by the time, and may be connected with the degradation of apparatus. Therefore, it is called for that the constituent for these adhesives is excellent in stability or creep resistance.

[0005]

A sealing material generally fills up the joined part and cravice between various members, and he is used in order to give watertight and airtightness. Therefore, since the flattery nature to the use part over a long period of time is very important, excelling in stability or endurance is called for as physical properties of a hardened material. Working joint of a building with an especially large change of joint width (Kasagi) the circumference of glass, the circumference of a window frame and a sash, a curtain wall, and various face panels — business — stability and endurance excellent in the constituent used for a sealing material, the sealing material for direct grazing, the sealing material for multiple glass, the sealing material for speed signal generator construction methods, etc. are called for.

[0006]

On the other hand, (the patent documents 1), (the patent documents 2), (the patent documents 3), the (patent documents 4), (The patent documents 5), the (patent documents 6), the (patent documents 7), the (patent documents 8), (The patent documents 9), the (patent documents 10), the (patent documents 11), the (patent documents 12), (The patent documents 13), the (patent documents 14), the (patent documents 15), the (patent documents 16), (The patent documents 17), the (patent documents 18), the (patent documents 19), the (patent documents 20), In (the patent documents 21), the (patent documents 22), the (patent documents 23), the (patent documents 24), the (patent documents 25), the (patent documents 26), the (patent documents 27), the (patent documents 28), and the (patent documents 29). Although the room-temperature-curing nature constituent which uses as an essential ingredient the organic polymer which has the reactive silicon group which three hydrolytic bases combined on silicon is indicated, In these advanced technology, the fast curability based on the reactive silicon group which three hydrolytic bases combined is mainly indicated, and the description which suggests stability, creep resistance, and endurance is not indicated.

[Patent documents 1] JP,H10-245482,A
[Patent documents 2] JP,H10-245484,A
[Patent documents 3] JP,H10-251552,A
[Patent documents 4] JP,H10-324793,A
[Patent documents 5] JP,H10-330630,A
[Patent documents 6] JP,H11-12473,A
[Patent documents 7] JP,H11-12480,A
[Patent documents 8] JP,H11-21463,A
[Patent documents 9] JP,H11-29713,A
[Patent documents 10] JP,H11-49969,A
[Patent documents 11] JP,H11-49970,A
[Patent documents 12] JP,H11-116831,A
[Patent documents 13] JP,H11-124509,A

[Patent documents 14] WO No. 47939 [98 to]
[Patent documents 15] JP,2000-34391,A
[Patent documents 16] JP,2000-109676,A
[Patent documents 17] JP,2000-109677,A
[Patent documents 18] JP,2000-109678,A
[Patent documents 19] JP,2000-129126,A
[Patent documents 20] JP,2000-129145,A
[Patent documents 21] JP,2000-129146,A
[Patent documents 22] JP,2000-129147,A
[Patent documents 23] JP,2000-136312,A
[Patent documents 24] JP,2000-136313,A
[Patent documents 25] JP,2000-239338,A
[Patent documents 26] JP,2001-55503,A
[Patent documents 27] JP,2001-72854,A
[Patent documents 28] JP,2001-72855,A
[Patent documents 29] JP,2000-327771,A
[Description of the Invention]
[Problem(a) to be Solved by the Invention]
[0007]
An object in view of the above-mentioned actual condition of this invention is to provide the stability, andurance, and creep resistance corrective strategy of a hardened material. The adhesives for interior panels with which stability, endurance, and creep rasistance have been improved as for this invention, The adhesives for face panels, the adhesives for tiling, the adhesives for stone tensions, ceiling finishing adhesives, Floor finishing adhesives, the adhesives for finishing of wall, the adhesives for car panels, the electrical and electric equipment, an electron and the adhesives for precision-mechanical-equipment assemblies, It aims at providing the sealing material for direct grazing, the sealing material for multiple glass, the sealing material for speed signal generator construction methods, or the sealing material for working joint of a building. An object of this invention is to provide the hardenability constituent which can give the hardened material excellent in stability, endurance, and creep resistance.
[Means for Solving the Problem]
[0008]
By using on silicon a silicon containing functional group which has three or more hydrolytic bases as a reactive silicon group of this polymar, as a result of inquiring wholeheartedly, in order that this invention persons may solve such a problem, It found out improving stability, endurance, and creep resistance, and this invention was completed.
[0009]
. Namely, the 1st of this invention has three or more hydrolytic bases on silicon. It has a silicon containing functional group which can conatruct a bridge by forming a siloxane bond, an organic polymer (A1) which is at least one sort as which a principal chain skeleton is chosen from an acrylic ester system copolymer obtained by polyoxyalkylene series polymer, saturated hydrocarbon system polymer, and a living-radical-polymerization method (meta-) — and
A silanol condensation catalyst which is at least one sort chosen from carboxylic acid tin salt (C), an organic tin catalyst (D), and a non-tin catalyst (E)
It is related with a containing hardenability constituent.
[0010]
A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is a general formula (6) :

$-Si(OR^4)_3$ (6)

It is related with said hardenability constituent characterized by what is expressed with (inside of formula and three R^4 is an organic group of monovalence of the carbon numbers 2-20 independently, respectively).
[0011]
A silicon containing functional group which can construct a bridge by forming a siloxane bond as a desirable embodiment is related with said hardenability constituent being a triethoxy allyl group.

[0012]
An organic polymar in which an organic polymer (A1) introduced an unsaturation group into an end as a desirable embodiment, and general formula (2) :

$H-SiX_3$ (2)

(X show a hydroxyl group or a hydrolytic basis among a formula, and three X may be the same and may differ.) — it is related with said hardenability constituent being an organic polymer obtained by an addition reaction with a hydrosilane compound expressed.
[0013]
An organic polymer in which an organic polymer (A1) introduced an unsaturation group into an end as a desirable embodiment, and general formula (9) :

$H-Si(OR^4)_3$ (9)

It is related with said hardenability constituent being an organic polymer obtained by an addition reaction with a hydrosilane compound expressed with (inside of formula and three R^4 is an organic group of monovalence of the carbon numbers 2-20 independently, respectively).
[0014]
As a desirable embodiment, an organic polymer (A1) is related with said hardenability constituent being an organic polymer which does not contain an amide segment (-NH-CO-) substantially in a principal chain skeleton.
[0015]
As a desirable embodiment, a silanol condensation catalyst is carboxylic acid tin salt (C), and it is related with said hardenability constituent containing an amine compound further.
[0016]
It is related with said hardenability constituent further characterized by containing an organic tin catalyst (D) as a desirable embodiment.
[0017]
An organic tin catalyst (D) as a desirable embodiment Dialkyl tin carboxylate, Dialkyl tin oxide and $Q_gSn(OZ)_{4-g}$ and $[Q_gSn(OZ)]_2O$ (among a formula) Z expresses an organic group which has a functional group with which Q can form a coordinate bond in an inside of a hydrocarbon group of monovalence of the carbon numbers 1-20, or self for a hydrocarbon group of monovalence of the carbon numbers 1-20 to Sn. g is 0, 1, 2, or 3. It is related with said hardenability constituent being at least one sort chosen from a group which consists of a compound shown.
[0018]
As a desirable embodiment, a carbon atom in which carboxylic acid tin salt (C) adjoins a carbonyl group is related with said hardenability constituent being the carboxylic acid tin salt (C1) which is the 4th class carbon.
[0019]
As a desirable embodiment, said non-tin catalyst (E) is carboxylic acid, and it is related with said hardenability constituent containing amine further.
[0020]
As a desirable embodiment, a carbon atom in which carboxylic acid adjoins a carbonyl group is related with said hardenability constituent being carboxylic acid which is the 4th class carbon.
[0021]
It is related with said hardenability constituent further characterized by containing a minute hollow body (F) as a desirable embodiment.
[0022]
It is related with said hardenability constituent characterized by an organic polymer (A1) being 5 to 28 % of the weight in a total amount of a hardenability constituent as a desirable embodiment.
[0023]
It is related with said hardenability constituent further characterized by containing epoxy resin (I) as a desirable embodiment.
[0024]
It is related with said hardenability constituent further characterized by containing silicate (B) as a desirable embodiment.
[0025]

As a desirable embodiment, silicate is related with said hardenability constituent being a condensate of tetra alkoxysilane.
[0026]
As a desirable embodiment, it is a general formula further (7). :

$-SiR^5_e(OR^6)_{3-e}$ (7)

(e R^6 is an organic group of monovalence of the carbon numbers 1-20 independently among a formula, respectively, and 3-e R^5.) It is an organic group of monovalence of the carbon numbers 2-20 independently, and e shows 0, 1, or 2, respectively. It is related with said hardenability constituent containing an aminosilane coupling agent (G) which has a basis expressed.
[0027]
It is related with said hardenability constituent, wherein a basis expressed with the above-mentioned general formula (7) is a triethoxy silyl group as a desirable embodiment.
[0028]
As a desirable embodiment, it is a general formula (6). :

$-Si(OR^4)_3$ (6)

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond expressed with (inside of formula and three R^4 is an organic group of monovalence of the carbon numbers 2-20 independently, respectively), and general formula (8) :

$-SiR^7_d(OCH_3)_e(OR^8)_{3-d-e}$ (8)

(d R^7 is an organic group of monovalence of the carbon numbers 1-20 independently among a formula, respectively, R^8 of a 3-d-e individual is an organic group of monovalence of the carbon numbers 2-20 independently, respectively, d shows 0, 1, or 2, and e shows 1, 2, or 3.) However, 3-d-e>=0 shall be satisfied. It is a hardenability constituent containing an aminosilane coupling agent (H) which has a basis expressed, and is related with said hardenability constituent recuperating oneself beforehand in this hardenability constituent.
[0029]
The 2nd general formula (6) of this invention :

$-Si(OR^4)_3$ (6)

An organic polymer which has a silicon containing functional group which can construct a bridge by forming a siloxane bond expressed with (inside of formula and three R^4 is an organic group of monovalence of the carbon numbers 2-20 independently, respectively), General formula (10) obtained by carrying out the ester exchange reaction of the compound (J) which has at least one methoxy group which can carry out an ester exchange reaction to an R^4O-basis of a general formula (6) :

$-Si(OCH_3)_f(OR^4)_{3-f}$ (10)

(among a formula, 3-f R^4 is an organic group of monovalence of the carbon numbers 2-20 independently, respectively, and f shows 1, 2, or 3.) — it is related with a manufacturing method of an organic polymer having a silicon containing functional group which can construct a bridge by forming a siloxane bond expressed.
[0030]
an organic polymer obtained with said manufacturing method as a desirable embodiment — and A silanol condensation catalyst which is at least one sort chosen from carboxylic acid tin salt (C), an organic tin catalyst (D), and a non-tin catalyst (E)
It is related with a containing hardenability constituent.
[0031]
It is related with an object for interior panels characterized by containing said hardenability constituent as a desirable embodiment, an object for face panels, or adhesives for car panels.
[0032]
It is related with a sealing material for working joint of a building characterized by containing said hardenability constituent as a desirable embodiment.
[0033]
Hereafter, this invention is explained in detail.

[0034]
Restriction in particular does not have a principal chain skeleton of an organic polymer (A) which has a reactive silicon group used for this invention, and it can use a thing with various kinds of principal chain skeletons.
[0035]
Specifically A polyoxyethylene, polyoxypropylene, polyoxy butylene, Polyoxy tetramethylen, a polyoxyethylene polyoxypropylene copolymer, Polyoxyalkylene series polymers, such as a polyoxypropylene polyoxy butylene copolymer; An ethylene-propylene system copolymer, A copolymer of polyisobutylene, isobutylene, isoprene, etc., polychloroprene, A copolymer with polyisoprene, isoprene or butadiene, acrylonitrile, styrene, etc., A copolymer with polybutadiene, isoprene or butadiene, acrylonitrile, styrene, etc., Hydrocarbon system polymers, such as a hydrogenation polyolefin system polymer produced by hydrogenating these polyolefine system polymers; Condensation with dibasic acid, such as adipic acid, and glycol, Or a polyester system polymer obtained by ring opening polymerization of lactone; Ethyl (meta) acrylate, An acrylic ester system copolymer produced by carrying out the radical polymerization of the monomers, such as butyl (meta) acrylate (meta); (meta) An acrylic ester system monomer, vinyl acetate, acrylonitrile, A vinyl-base polymer produced by carrying out the radical polymerization of the monomers, such as styrene; A vinyl monomer in inside of said organic polymer is polymerized. Graft polymer; obtained. Polysulfide system polymer; Nylon 610 by condensation polymerization of nylon 6 by ring opening polymerization of epsilon caprolactam, hexamethylenediamina, Nylon 66 by condensation polymerization of adipic acid and hexamathylenediamine, and sebacic acid, Nylon 11 by condensation polymerization of epsilon-aminoundecanoic acid, A polycarbonate system polymer manufactured by carrying out condensation polymerization from polyamide system polymer, for example, bisphenol A, and carbonyl chlorides which have a two or more-ingredient ingredient among Nylon 12 by ring opening polymerization of epsilon-amino RAURO lactam, and the above-mentioned nylon, such as copolyamide, A diallyl phthalate system polymer etc. are illustrated. A polyoxyalkylene series polymer, a hydrocarbon system polymer, a polyester system polymer, an acrylic ester (meta) system copolymer, a polycarbonate system polymer, etc. are preferred from acquisition and manufacture being easy among polymers with the above-mentioned principal chain skeleton.
[0036]
Saturated hydrocarbon system polymers, such as polyisobutylene, hydrogenation polyisoprene, and hydrogenation polybutadiene, and a polyoxyalkylene series polymer and an acrylic ester (meta) system copolymer have a comparatively low glass transition temperature, and their hardened material obtained is preferred especially from excelling in cold resistance.
[0037]
In a principal chain skalaton of the above-mentioned organic polymer (A), other ingredients, such as a urethane bond ingredient, may be included in the range which does not spoil an affect of this invention greatly.
[0038]
It is not limited especially as the above-mentioned urethane bond ingredient, but For example, toluene (tolylene) diisocyanate, Aromatic system polyisocyanates, such as diphenylmethane diisocyanate and xylylene diisocyanate; Isophorone diisocyanate, What is obtained from a reaction of polyisocyanate compounds, such as aliphatic series system polyisocyanates, such as hexamethylene di-isocyanate, and polyol which has various kinds of above-mentioned principal chain skeletons can be mentioned.
[0039]
If there are many amide segments (-NH-CO-) generated in a principal chain skeleton based on said urethane bond, viscosity of an organic polymer will become high and will serve as a bad constituent of workability. Therefore, as for quantity of an amide segment occupied in a principal chain skeleton of an organic polymer, it is preferred that it is 3 or less % of the weight, it is more preferred that it is 1 or less % of the weight, and it is most preferred that an amide segment is not included substantially.
[0040]
A reactive silicon group contained in an organic polymer which has a reactive silicon group is a basis which can oonstruct a bridge by forming a siloxane bond by the reaction which has a hydroxyl group or a hydrolytic basis oombined with a silicon atom, and is accelerated by a silanol condensation

catalyst. As a reactive silicon group, it is a general formula (11). :

$-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (11)

an alkyl group of the carbon numbers 1–20 from which R^1 in a formula and R^2 were the same as or different. When the Tori ORGANO siloxy group shown by aryl group of the carbon numbers 6–20, an aralkyl group of the carbon numbers 7–20, or $(R')_3SiO-$ is shown and R^1 or two or more R^2 exist, they may be the same and may differ. R' is a hydrocarbon group of monovalence of the carbon numbers 1–20 here, and three R' may be the same and may differ. X shows a hydroxyl group or a hydrolytic basis, and when two or more X exists, they may be the same and may differ. As for a, 0, 1, 2, or 3b shows 0, 1, or 2, respectively. About b in m bases ($SiR^1_{2-b}X_bO$), they may be the same and may differ. m shows an integer of 0 to 19, however — what satisfies a+sigma b>=1 — carrying out — a basis expressed is raised.

[0041]

It is not limited but what is necessary is just a conventionally publicly known hydrolytic basis especially as a hydrolytic basis. Specifically, a hydrogen atom, a halogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an acid–amide group, an aminooxy group, a sulfhydryl group, an alkenyloxy group, etc. are mentioned, for example. Among these, a hydrogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an aminooxy group, a sulfhydryl group, and an alkenyloxy group are preferred. hydrolysis nature is quiet and a viewpoint of handling or a cone to especially an alkoxy group is preferred.

[0042]

A hydrolytic basis and a hydroxyl group can be combined with one silicon atom in the 1–3 ranges, and (a+sigmab) has 1–5 preferred ranges. When a hydrolytic basis and a hydroxyl group join together in [two or more] a reactive silicon group, they may be the same and may differ.

[0043]

In particular, it is a general formula (12). :

$-SiR^2_{3-a}X_a$ (12)

(R^2 and X are the same as the above among a formula.) Since a reactive silicon group expressed with an integer of 1–3 is easy to receive, a's is preferred.

[0044]

As an example of R^1 in the above–mentioned general formula (11) and (12), and R^2. For example, aralkyl groups, such as aryl groups, such as cycloalkyl groups, such as alkyl groups, such as a methyl group and an ethyl group, and a cyclohexyl group, and a phenyl group, and benzyl, the Tori ORGANO siloxy group R' is indicated to be by $(R')_3SiO-$ which is a methyl group, a phenyl group, etc. (R'), etc. are raised. Especially in these, a methyl group is preferred.

[0045]

As more concrete illustration of a reactive silicon group, a trimethoxysilyl group, a triethoxy silyl group, a triisopropoxy silyl group, a dimethoxymethyl silyl group, a diethoxymethylsilyl group, and a diisopropoxy methyl silyl group are mentioned.

[0046]

Especially in this invention, an organic polymer which has the silicon containing functional group (that is, the number of a+bxm of a general formula (11) is three or more) which three or more hydrolytic bases combined on silicon in an organic polymer of the (A) ingredient can be used as an ingredient (A1).

[0047]

A hardened material which three or more hydrolytic bases had combined this (A1) ingredient on silicon, and constructed the bridge by a silanol condensation reaction of that reactive silicon group, Good stability is shown and remarkable creep resistance and an endurance improvement effect are shown as compared with a case of reactive silicon group containing organic polymer which has two or less hydrolytic bases.

[0048]

(A1) As for the number of a+bxm of a general formula (11) of an ingredient, it is more preferred that it

is 3–5, and especially 3 is preferred. Also in it, since [that its improvement effect of the stability of a hardenability constituent of this invention, endurance, and creep resistance is especially large and] the Tori alkoxy silyl groups has the good availability of a raw material, it is preferred. Thing of an alkoxyl group of the carbon numbers 1–20 is preferred, its thing of the carbon numbers 1–10 is more preferred, and its thing of the carbon numbers 1–4 is still more preferred here. Specifically, a trimethoxysilyl group and a triethoxy silyl group are the most preferred. Hardenability may beoome late when a carbon number is larger than 20.

[0049]

Generally, if weight % of reactive silicon group containing organic polymer in a hardenability constituent becomes low, it is known that the endurance of a hardened material obtained will fall to **. However, if an ingredient (A1) of this invention is used as reactive silicon group containing organic polymer, high endurance is maintainable even if it makes low weight % of reactive silicon group containing organic polymer in a hardenability constituent. Therefore, five to 28% of the weight, when it is 15 to 24 % of the weight especially preferably, since a rate of an ingredient (A1) in a hardenability constituent is compatible in low cost and high endurance, it is more preferably preferred [rate] ten to 26% of the weight.

[0050]

Especially in this invention, an organic polymer which has the Tori alkoxy silyl groups of the carbon numbers 2–20 can be used as a (A4) ingredient in an organic polymer of an ingredient (A1). Namely, general formula (6) :

$-Si(OR^4)_3$ (6)

(three R^4 is the organic groups of monovalence of the carbon numbers 2–20 independently among a formula, respectively.) — an organic polymer which has a basis expressed can be used as a (A4) ingredient.

[0051]

It is known that methanol generated in connection with a hydrolysis reaction of a methoxy silyl group has peculiar toxicity of causing an obstacle of an optic nerve. On the other hand, since a carbon number of an alkoxy group which combines the (A4) ingredient with a silicon atom is 2 to 20, toxic high methanol is not contained in alcohol generated in connection with a hydrolysis reaction of a reactive silicon group, but serves as a constituent with high safety at it.

[0052]

(A4) It is preferred that it is especially 2–4, and when it is 2, it serves as ethanol, and since alcohol generated by hydrolysis has the highest safety, it is the most preferred [as for a carbon number of R^4 of a general formula (6) of an ingredient, it is more preferred that it is 2–10, and / alcohol]. Specifically, a triethoxy silyl group is the most preferred. When a carbon number is larger than 20, while the hardenability of a hardenability constituent may become late, an anaesthetic action and stimulation of alcohol to generate may be large.

[0053]

Especially in this invention, a principal chain skeleton can use as a (A5) ingredient what is polyoxyalkylene in an organic polymer of the (A4) ingredient. Namely, general formula (6) :

$-Si(OR^4)_3$ (6)

A polyoxyalkylene series polymer which has a basis expressed with (R^4 in a formula is the same as the above) can be used as a (A5) ingredient.

[0054]

1.1–5 reactive silicon groups of an organic polymer (A) exist preferably [that average per molecule and at least one piece exists], and more preferably, If the number of reactive silicon groups contained in one molecule of organic polymers (A) will be less than one piece, hardenability will become insufficient and will become difficult to reveal a good rubber elasticity action. A reactive silicon group may exist in an end of an organic polymer (A) chain, and may exist in an inside. Since effective network chain density of an organic polymer (A) ingredient contained in a hardened material formed eventually will increase if a reactive silicon group exists in an end of a chain, a rubber–like hardened material in which a low elastic modulus is shown becomes is easy to be obtained by high intensity and high elongation.

[0055]

Especially in this invention, an organic polymer the number of reactive silicon groups per molecule averages, and 1.7-5 pieces exist in an organic polymer of the (A) ingredient can be used as an ingredient (A2).

[0056]

A hardened material which the number of reactive silicon groups per molecule averaged this (A2) ingredient for it, and 1.7-5 pieces existed, and constructed the bridge by a silanol condensation reaction of that reactive silicon group. Good stability is shown, the number of reactive silicon groups per molecule averages, and remarkable creep resistance and an endurance improvement effect are shown as compared with a case of less than 1.7 organic polymers.

[0057]

(A2) As for the number of reactive silicon groups per molecule of an ingredient, it is more preferred that they are 2-4 pieces, and it is preferred that they are especially 2.3-3 pieces. When there are few 1.7 reactive silicon groups per molecule, an improvement effect of the stability of a hardenability constituent of this invention, endurance, and creep resistance may not be enough, and when larger than five pieces, elongation of a hardened material obtained may become small.

[0058]

Especially at this invention, it is a general formula in an organic polymer of the (A) ingredient (3). :

$-O-R^3-CH(CH_3)-CH_2-(SiR^1_{2-b}X_bO)_m-SiR^2_{3-a}X_a$ (3)

(R^3 in a formula a divalent organic group of the carbon numbers 1-20 which contain one or more sorts chosen from a group which consists of hydrogen, oxygen, and nitrogen as a composition atom) [show and] R^1, R^2, X, a, b, and m -- the above -- it is the same -- an organic polymer which has a structure part with which it is expressed can be used as a (A3) ingredient.

[0059]

A hardened material which this (A3) ingredient has a structure part expressed with a general formula (3), and constructed the bridge by a silanol condensation reaction of that reactive silicon group shows good stability, and shows remarkable creep resistance and an endurance improvement effect as compared with a case of an organic polymer which has terminal structures other than a general formula (3).

[0060]

As for a carbon number of R^3 of a general formula (3), it is more preferred from a point of availability that it is 1-10, and it is preferred that it is especially 1-4. Specifically, R^3 has the most preferred methylene group.

[0061]

(A3) An ingredient is genaral formula (5). :

$-O-R^3-CH(CH_3)-CH_2-SiX_3$ (5)

(R^3 in a formula and X are the same as the above.) -- when it is an organic polymer which has a structure part with which it is expressed, since [that an improvement effect of the stability of a hardenability constituent of this invention, endurance, and craap resistance is especially large and] the availability of a raw material is good, it is desirable.

[0062]

(A) What is necessary is just to perform introduction of a reactive silicon group of an ingredient by a publicly known method. That is, the following methods are mentioned, for example.

[0063]

(b) Make an organic compound which has an active group and an unsaturation group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, in a molecule to this functional group react, and obtain an organic polymer containing an unsaturation group. Or an unsaturation group content organicity polymer is obtained by copolymerization with an unsaturation group content epoxy compound. Subsequently, hydrosilane which has a reactive silicon group is made to act on an acquired resultant, and it hydrosilylates.

[0064]

(**) Make a compound which has a sulfhydryl group and a reactive silicon group react to an organic polymer containing an unsaturation group produced by making it be tha sama as that of the (b) method.

[0065]

(**) Make a compound which has a funotional group and a reactive silicon group which show reactivity to an organic polymer which has functional groups, such as a hydroxyl group, an epoxy group, and an isocyansta group, in a molacule to this functional group react.

[0066]

Since a high inversion rate is obtained in comparatively short reaction time, a method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group react to an end a method of (b) or among (**)s in the above method is preferred. An organic polymer which has the reactive silicon group obtained by a method of (b), (**) Since becoming a good hardenability constituent of workability by hypoviscosity rather than an organic polymer obtained by a method and an organic polymer obtained by a method of (**) have the strong bad smell based on an mercaptosilane, especially its method of (b) is preferred.

[0067]

(b) As an example of a hydrosilane compound used in a method, For example, trichlorosilane, methyldi chlorosilicane, dimethylchlorosilicane, Halogenation Silang like phenyl dichlorosilane; Trimethoxysilane, Triethoxysilane, methyldiethoxysilane, methyl dimethoxysilane, The alkoxysilane like phenyl dimethoxysilane; Methyldi acetoxysilane, The acyloxy silanes like a phenyldiacetoxysilane; although the KETOKISHI mate silanes like bis(dimethyl KETOKISHI mate)methylsilane and bis(cyclohexyl KETOKISHI mate)methylsilane are raised, it is not limited to these. Especially among these, halogenation Silang and alkoxysilane are preferred, especially alkoxysilane has the quiet hydrolysis nature of a hardenability constituent obtained, and it is the most preferred to a handling and cone sake.

[0068]

In the above-mentioned hydrosilane compound, it is a general formula (2). :

$H-SiX_3$ (2)

Since a hydrosilane compound expressed with (X in a formula is the same as the above) has an especially large improvement effect of the stability of a hardenability constituent which consists of an organic polymer obtained by an addition reaction of this hydrosilane compound, endurance, and creep resistance, it is preferred. In a hydrosilane compound expressed with a general formula (2), trialkoxysilane, such as trimethoxysilane, triethoxysilane, and a triisopropoxy silane, is more preferred.

[0069]

trialkoxysilane in which carbon numbers, such as trimethoxysilane, have an alkoxy group (methoxy group) of 1 also in said trialkoxysilane is like [when disproportionation may advance quickly and disproportionation progrssses] dimethoxysilane -- a dangerous compound arises in inside. From a viewpoint of safaty on handling to a general formula (9) :

$H-Si(OR^4)_3$ (9)

It is preferrad to use trialkoxysilane which has an alkoxy group whose carbon number expressed with (R^4 in a formula is the same as the above) is two or more. A viewpoint of availability, safety [on handling], stability [of a hardenability constituent obtained], endurance, and creep resistance ** to triethoxysilane is the most preferred.

[0070]

(**) Although a method of introducing into an unsaturation binding site of an organic polymer a compound which has a sulfhydryl group and a reactive silicon group as a synthetic method by a radical addition reaction under a radical initiator and/or radical source-of-release existence, for example, etc. are mentioned, it is not limited in particular. As an example of a compound of having said sulfhydryl group and a reactive silicon group, For example, although gamma-mercapto propyltrimethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, gamma-mercaptopropyl triethoxysilane, gamma-mercapto propylmethyl diethoxysilane, etc. are raised, it is not limited to these.

[0071]

(**) Although a method etc. which are shown in JP,H3-47825,A are mentioned, for example as a method of making a compound which has a polymer, an isocyanate group, and a reactive silicon group which have a hydroxyl group reacting to an end among synthetic methods, it is not limited in

particular. As an example of a compound of having said isocyanate group and a reactive silicon group, For example, although gamma-isocyanate propyltrimethoxysilane, gamma-isocyanate propylmethyl dimethoxysilane, gamma-isocyanatopropyl triethoxysilane, gamma-isocyanato propylmethyl diethoxysilane, etc. are raised, it is not limited to these.
[0072]
As mentioned above, as for a silane compound which three hydrolytic bases have combined with one silicon atoms, such as trimethoxysilane, disproportionation may advance, As for trialkoxysilane in which especially carbon numbers, such as trimethoxysilane, have an alkoxy group (methoxy group) of 1, disproportionation may advance quickly. If disproportionation progresses, a remarkable dangerous compound [like] which is dimethoxysilane will arise. However, such disproportionation advances in neither gamma-mercapto propyltrimethoxysilane nor gamma-isocyanate propyltrimethoxysilane. For this reason, when using the Tori alkoxy silyl groups which has methoxy groups, such as a trimethoxysilyl group, as a silicon content group, it is preferred to use a synthetic method of (**) or (**).
[0073]
As how to obtain an organic polymer which has the silicon content group combined with a methoxy group, it is one method of the above-mentioned (**), (**), and (**), and a reactive silicon group is a general formula (6). :

$$-Si(OR^4)_3 \quad (6)$$

A compound (J) which has at least one methoxy group which can carry out an ester exchange reaction after obtaining an organic polymer (getting it blocked the above-mantioned (A4) ingredient) which has a basis expressed with (R^4 in a formula is the same as the above), it is a general formula by carrying out an ester exchange reaction under existence of a transesterification catalyst or nonexistence (10). :

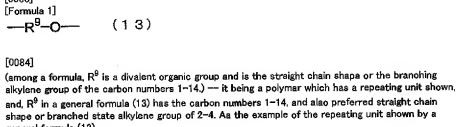
$$-Si(OCH_3)_f(OR^4)_{3-f} \quad (10)$$

(among a formula, 3-f R^4 is the organic groups of monovalence of the carbon numbers 2-20 independently, respectively, and f shows 1, 2, or 3.) — a method of manufacturing an organic polymer which has a basis expressed can be mentioned. An organic polymer which has a basis expressed with a general formula (10) shows fast curability rather than an organic polymer which has a basis expressed with a general formula (6).
[0074]
In said manufacturing method, after introducing a reactive silicon group especially by a method of (**), by carrying out an ester exchange reaction to the aforementioned (J) ingredient, A method of manufacturing an organic polymer which has a basis expressed with a general formula (10), Without a dangerous compound like dimethoxysilane by disproportionation arising in the middle of manufacture, there are few bad smells, and also since it becomes a good hardenability constituent of workability by hypoviscosity rather than an organic polymer obtained by a method of (**), it is more desirable than an organic polymer obtained by a method of (**).
[0075]
As a compound (J) which has at least one above-mentioned methoxy group which can carry out an ester exchange reaction, there is no limitation in particular and various kinds of compounds can be used.
[0076]
A compound etc. which have the silicon atom combined with methyl ester of various kinds of acid, such as methanol, carboxylic acid, and sulfonic acid, and at least one methoxy group as a (J) ingredient here can be mentioned. Since a compound which has the silicon atom united with 2-4 methoxy groups on the same silicon atom as a compound which has the silicon atom combined with said at least one methoxy group has a quick ester exchange reaction speed, it is preferred. Since especially a compound that has a silicon atom united with 2-4 methoxy groups on the same silicon atom and an amino group has a quick ester exchange reaction speed, it is preferred.
[0077]
When it illustrates concretely, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, Amino group content Silang, such as gamma-ureido

propyltrimethoxysilane, N-phenyl-gamma-aminopropyl trimathoxysilane, and N-benzyl-gamma-aminopropyl trimethoxysilane, can be mentioned. A denatured derivative and a condensation reaction thing of the above-mentioned silane compound can also use the above-mentioned silane compound as a (J) ingredient.
[0078]
Since an ester exchange reaction advances also under existence of a transesterification catalyst and comparatively low temperature conditions 80 ** or less, aforementioned amino group content Silang is preferred.
[0079]
As for the (J) ingredient used for this invention, it is preferred to use and carry out an ester exchange reaction in 0.1-10 copies to 100 copies of reactive silicon group containing organic polymer of the (A4) ingredient. It is preferred to use it in 1-5 copies especially. The above-mentioned (J) ingredient may be used only by one kind, and may carry out two or more kind mixing use.
[0080]
An organic polymer (A) which has a reactive silicon group may have straight chain shape or branching, and the number average molecular weight is 1,000-30,000 more preferably 500 to about 50,000 in polystyrene conversion in GPC. When there is a tendency whose number average molecular weight is inconvenient in respect of the extension characteristic of a hardened material at less than 500 and 50000 is exceeded, since it becomes hyperviscosity, there is an inconvenient tendency in respect of workability.
[0081]
A reactive silicon group may be in an end or an inside of an organic polymer chain, and may be in both. Since effective network chain density of an organic polymer component contained in a hardened material formed eventually increases especially when a reactive silicon group is in a molecular terminal, it is desirable from points, like a rubber-like hardened material of high elongation becomes is easy to be obtained with high intensity.
[0082]
Said polyoxyalkylene series polymer is a general formula intrinsically (13). :
[0083]
[Formula 1]

$$-R^8-O- \quad (13)$$

[0084]
(among a formula, R^8 is a divalent organic group and is the straight chain shape or the branching alkylene group of the carbon numbers 1-14.) — it being a polymar which has a repeating unit shown, and, R^8 in a general formula (13) has the carbon numbers 1-14, and also preferred straight chain shape or branched state alkylene group of 2-4. As the example of the repeating unit shown by a general formula (13),
[0085]
[Formula 2]



[0086]

** is mentioned. The principal chain skeleton of a polyoxyalkylene series polymer may consist of one kind of repeating unit, and may consist of two or more kinds of repeating units. When used especially for sealant etc., it is desirable from that what comprises the polymer which usas a propylene oxide polymer as the main ingredients is amorphous, or the point which is hypovicosity comparatively.
[0087]
As a synthetic method of a polyoxyalkylene series polymer, For example, the polymerizing method by an alkali catalyst like KOH, the polymerizing method by a transition metal compound-porphyrin complex catalyst like a complex produced by making an organoaluminium compound and porphyrin which are shown in JP,61-215623,A react, JP,49-27250,B, JP,59-15336,B, a U.S. Pat. No. 3278457 item, a U.S. Pat. No. 3278458 item, A U.S. Pat. No. 3278459 item, a U.S. Pat. No. 3427256 item, a U.S. Pat. No. 3427334 item, The polymerizing method by a composite metal cyanide complex catalyst shown in a U,S. Pat. No. 3427335 item etc., **********, such as the polymerizing method using a catalyst which consists of a polyphosphazene salt illustrated by JP,H10-273512,A, and the polymerizing method using a catalyst which consists of a phosphazene compound illustrated by JP,H11-060722,A, are not limited in particular.
[0088]
A manufacturing method of a polyoxyalkylene series polymer which has a reactive silicon group, JP,45-36319,B, 46-12154, JP,50-156599,A, 54-6096, 55-13767, 55-13468, What is proposed by each gazette, such as 57-164123, JP,3-2450,B, U.S. Pat. No. 3632557, U.S. Pat. No. 4345053, U.S. Pat. No. 4366307, and U.S. Pat. No. 4960844, JP,61-197631,A, 61-215622, 61-215623, Although 6,000 or more number average molecular weights and Mw/Mn which are proposed by each gazette of 61-218632, JP,H3-72527,A, JP,H3-47825,A, and JP,H8-231707,A can illustrate a polyoxyalkylene series polymer with narrow molecular weight distribution in the 1.6 or less amount of Polymer Division, It is not limited to in particular these.
[0089]
A polyoxyalkylene series polymer which has the above-mentioned reactive silicon group may be used alone, and may be used together two or more sorts.
[0090]
Said saturated hydrocarbon system polymer is a polymer which does not contain substantially carbon-carbon unsaturated bonds other than an aromatic ring, and a polymer which makes the skeleton, (1). [whether an olefinic compound of the carbon numbers 1-6, such as ethylene, propylene, 1-butene, and isobutylene, is polymerized as a main monomer, and] (2) After making diene series, such as butadiene and isoprene, homopolymerize or carrying out copolymerization of the above-mentioned olefinic compound. can obtain by a method of hydrogenating, but. Since an isobutylene system polymer and a hydrogenation polybutadiene system polymer tend to introduce a functional group into an end, and tend to control a molecular weight and can increase tha number of and functional groups, they are preferred, and a composite easa to especially their isobutylene system polymer is preferred.
[0091]
That whose principal chain skeleton is a saturated hydrocarbon system polymer has the feature which is excellent in heat resistance, weatherability, endurance, and humidity interception nature.
[0092]
All the monomeric units may be formed from an isobutylene unit, and an isobutylene system polymer, Although a copolymer with other monomers may be sufficient, what contains a repeating unit which originates in isobutylene from a field of rubber property 50% of the weight or more is preferred, what is contained 80% of the weight or more is more preferred, and especially a thing contained 90 to 99% of the weight is preferred.
[0093]
As a synthetic method of a saturated hydrocarbon system polymer, although various polymerization methods are reported conventionally, especially living polymerization what is called of recent years many is developed. an iniphor polymerization (J. — P.Kennedy et al.,) which was found out by Kennedy and others in the case of a saturated hydrocarbon system polymer, especially an isobutylene system polymer J. Polymer Sci. and Polymer Chem. Ed. 1997, By using 15 volumes and 2843 pages, manufacturing easily is possible, about 500 to 100,000 molecular weight can be polymerized in 1.5 or less molecular weight distribution, and it is known that various functional groups

can be introduced into a molecular terminal.
[0094]
As a process of a saturated hydrocarbon system polymer which has a reactive silicon group, For example, JP,4-69659,B, JP,7-108928,B, JP,63-254149,A, Although it writes in each Description of JP,64-22904,A, JP,1-197509,A, Patent Gazette No. 2539445, Patent Gazette No. 2873395, and JP,7-53882,A, it is not limited to in particular these.
[0095]
It is a general formula in a saturated hydrocarbon system polymer which has the above-mentioned reactive silicon group (6). :
$-Si(OR^4)_3$ (6)
Especially (A7) a saturated hydrocarbon system polymer that has a basis expressed with (R^4 in a formula is the same as the above) can be used as an ingredient. This (A7) ingredient has the feature which is excellent in heat resistance based on a saturated hydrocarbon system polymer, weatherability, and humidity interception nature of a principal chain skeleton, and does not have generation of methanol accompanying a hydrolysis reaction of a reactive silicon group, and is a polymer whose stability of a hardened material, endurance, and creep resistance are still better.
[0096]
A saturated hydrocarbon system polymer which has the above-mentioned reactive silicon group may be used alone, and may be usad together two or more sorts.
[0097]
Especially in this invention, a chain can use what is an acrylic ester (meta) system copolymer as an ingredient (A8) in an organic polymer of the (A) ingredient.
[0098]
Especially as an acrylic ester (meta) system monomer which constitutes a main chain of the aforementioned (meta) acrylic ester system polymer, it is not limited but various kinds of things can be used. If it illustrates, acrylic acid (meta), methyl acrylate (meta), (Meta) Ethyl acrylate, acrylic acid (meta)-n-propyl, acrylic acid (meta) isopropyl, (Meta) Acrylic acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic acid-tert-butyl, acrylic acid (meta)-n-pentyl, (Meta) Acrylic acid-n-hexyl, acrylic acid (meta) cyclohexyl, (Meta) Acrylic acid-n-heptyl, acrylic acid (meta)-n-octyl, (Meta) Acrylic acid-2-ethylhexyl, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) Acrylic acid toluyl, acrylic acid (meta) benzyl, acrylic acid (meta)-2-methoxy ethyl, (Meta) Acrylic acid-3-methoxy butyl, acrylic acid (meta)-2-hydroxyethyl, (Meta) Acrylic acid-2-hydroxypropyl, acrylic acid (meta) stearyl, metaglycidyl acrylate (meta), acrylic acid (meta) 2-aminoethyl, gamma-(methacryloyl oxypropyl) trimethoxysilane, an ethyleneoxide addition of acrylic acid (meta), (Meta) Acrylic acid trifluoromethyl methyl, an acrylic acid (meta) 2-trifluoro methylethyl, (Meta) Acrylic acid 2-perfluoro ethylethyl, acrylic acid (mata) 2-perfluoro ethyl-2-perfluoro butylethyl, (Meta) Acrylic acid 2-perfluoro ethyl, acrylic acid (meta) perfluoro methyl, (Meta) Acrylic acid JIPA fluoromethylmathyl, acrylic acid (meta) 2-perfluoro methyl-2-perfluoro ethylmethyl, (Mata) Acrylic acid series (meta) monomers, such as acrylic acid 2-perfluoro haxylathyl, acrylic acid (meta) 2-perfluoro deoylethyl, and acrylic acid (meta) 2-perfluoro hexadecylethyl, etc. are mentioned. In the aforementioned (meta) acrylic ester system copolymer, copolymerization of the following vinyl system monomers can also be carried out with an acrylic ester (meta) system monomer. When this vinyl system monomer is illustrated, styrene, vinyltoluene, alpha-methylstyrene, Styrene system monomers, such as KURORU styrene, styrene sulfonic acid, and its salt; Perfluoro ethylene, Fluoride content vinyl monomers, such as perfluoro propylene and vinylidene fluoride; Vinyltrimetoxysilane, Silicon content vinyl system monomers, such as vinyltriethoxysilane; A maleic anhydride, Monoalkyl ester and dialkyl ester of maleic acid and maleic acid; Fumaric acid, Monoalkyl ester and dialkyl ester of fumaric acid; Maleimide, Methylmaleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexylmaleimide, octylmaleimide, dodecylmaleimide, stearyl maleimide, Maleimide system monomers, such as phenylmaleimide and cyclohexylmaleimide; Acrylonitrile, Nitrile group content vinyl system monomers, such as a methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Alkenes; butadiene, such as vinyl ester; ethylene, such as vinyl acetate, vinyl propionate, vinyl pivalate, banzoic acid vinyl, and vinyl cinnamic acid, and propylene, Conjugated dienes, such as isoprene; VCM/PVC, a vinylidene chloride, an allyl chloride, allyl alcohol, etc. are mentioned. These may be used independently, and even if it carriaa out copolymerization of the

plurality, they are not cared about. Especially, a polymer which consists of a styrene system monomer from physical properties etc. and (meta) an acrylic acid series monomer of output is preferred. It is an acrylic polymer which consists of acrylic ester monomer and a methacrylic-acid-ester monomer (meta) more preferably, is an acrylic polymer which consists of acrylic ester monomer preferably especially, and is a polymer which consists of butyl acrylates still more preferably. A point that physical properties, such as hypoviscosity of a compound, a low modulus of a hardened material, high elongation, weatherability, and heat resistance, are required in a use of general ******* to a butyl acrylate system monomer is still more preferred. A copolymer mainly concerned with ethyl acrylate on the other hand in a use as which oil resistance, such as an automotive application, etc. are required is still more preferred. It can also transpose a part of ethyl acrylate to butyl acrylate in order to raise that low-temperature characteristic, since it tends to be a little inferior to the low-temperature characteristic (cold resistance), although a polymer mainly concerned with this ethyl acrylate is excellent in oil resistance. However, since it follows on increasing a ratio of butyl acrylate and the good oil resistance is spoiled. as for the ratio, for a use of which oil resistance is required, it is preferred to carry out to 40% or less, and also it is more preferred to make it to 30% or less. In order to improve the low-temperature characteristic etc., without spoiling oil resistance, it is also preferred to use acrylic acid 2-methoxy ethyl, acrylic acid 2-ethoxyethyl, etc. by which oxygen was introduced into an alkyl group of a side chain. However, since it is in a tendency for heat resistance to be inferior by introduction of an alkoxy group which has an ether bond in a side chain, when heat resistance is required, it is prefarred [the ratio] to make it to 40% or less. It is possible to obtain a polymer which changed the ratio and was suitable in consideration of physical properties needed, such as oil resistance, heat resistance, and the low-temperature characteristic, according to a various application or the purpose demanded. For example, as an example which is excellent in properties balance, such as oil resistance, heat resistance, the low-temperature characteristic, although limitation is not carried out, a copolymer of ethyl acrylate / butyl acrylate / acrylic acid 2-methoxy ethyl (it is 40-50/20-30/30-20 at a weight ratio) is mentioned. In this invention, it is preferred other monomers. copolymerization, and also that may carry out block copolymerization and these desirable monomers are contained not less than 40% by a weight ratio in these desirable monomers in that case. Acrylic acid (meta) expresses acrylic acid and/, or methacrylic acid with the above-mentioned expressive form.

[0099]

(Meta) It is not limited but what is necessary is just to carry out by a publicly known method especially as a synthetic method of an acrylic ester system copolymer (A6). However, it has the problem that a polymer obtained by the usual free radical polymerizing method using an azo compound, a peroxide, etc. as a polymerization initiator generally has a value of molecular weight distribution as large as two or more. and viscosity becomes high. Therefore, molecular weight distribution is narrow, and in order to obtain an acrylic ester system copolymer which has a cross-linking functional group in molecular chain terminals at a high rate (meta), it is preferred [it is an acrylic ester system copolymer with low (meta) viscosity, and] to use a living-radical-polymerization method.

[0100]

Also in a "living-radical-polymerization method", an organic halogenated compound or a sulfonyl halide compound An initiator. An "atom-transfer-radical-polymerization method" which polymerizes an acrylic ester (meta) system monomer by making a transition metal complex into a catalyst. As a manufacturing method of an acrylic ester system copolymer which in addition to the feature of the above-mentioned "living-radical-polymerization method" has halogen comparatively advantageous to a functional group conversion reaction etc. at the end, and has a specific functional group from flexibility of a design of an initiator or a catalyst being large (meta), it is still more desirable. 117 volumes. 5614 pages. etc. will be mentioned as this atom-transfer-radical-polymerization method in Matyjaszewski et al. and journal OBU American chemical society (J. Am.Chem.Soc.) 1995.

[0101]

A hardened material produced by hardening a hardenability constituent containing an acrylic ester system copolymer which has a reactive silicon group (meta) may have low elongation as compared with a hardenability constituent containing an organic polymer which has other principal chain skeletons, such as a polyoxyalkylene series polymer. Even if it uses an acrylic ester (meta) system

copolymer manufactured using the above "living-radical-polymerization method" and an "atom-transfer-radical-polymerization method", elongation may be insufficient and endurance may be bad. As compared with an organic polymer which can improve notably the endurance of this (meta) acrylic ester system copolymer by using on silicon a silicon containing functional group which has three or more hydrolytic bases as a reactive silicon group, and has other principal chain skeletons, an endurance improvement affect is large.

[0102]

As a process of an acrylic ester system copolymer which has a reactive silicon group (meta), a process using the free radical polymerizing method for having used a chain transfer agent for JP,H3-14068,B, JP,H4-55444,B, JP,H6-211922,A, etc. is indicated. for example. Although a process which used an atom-transfer-radical-polymerization method for JP,H9-272714,A etc. is indicated. it is not limited to in particular these.

[0103]

It is a general formula in an acrylic ester system copolymer which has the above-mentioned reactive silicon group (meta) (6). :

$-Si(OR^4)_3$ (6)

especially (A6) an acrylic ester system copolymer that has a basis expressed with (R^4 in a formula is the same as the above) (meta-) can be used as an ingredient. Heat resistance based on an acrylic ester (meta) system copolymer of a principal chain skeleton in this (A6) ingredient, It has the feature which is excellent in weatherability and chemical resistance, and there is no generation of methanol accompanying a hydrolysis reaction of a reactive silicon group, and it is a polymer whose stability of a hardened material, endurance, and creep resistance are still better.

[0104]

A reactive silicon group of the aforementioned (A6) ingredient may be in an end or an inside of an organic polymer chain, and may be in both. Since effective network chain density of a polymer component contained in a hardened material formed eventually increases especially when a reactive silicon group is in an end of a polymer main chain, it is desirable from points, like a rubber-like hardened material of high elongation becomes is easy to be obtained with high intensity.

[0105]

As a polymerization method of the aforementioned (A6) ingredient, when a living-radical-polymerization method is used, since molecular weight distribution is narrow, it is hypoviscosity, and from the ability to introduce a cross-linking functional group into molecular chain terminals at a high rate, it is more desirable and especially an atom-transfer-radical-polymerization method is preferred.

[0106]

An acrylic ester system copolymer which has the above-mentioned reactive silicon group (meta) may be used alone, and may be used together two or more sorts.

[0107]

An organic polymer which has these reactive silicon groups may be used alone, and may be used together two or more sorts. Specifically, a polyoxyalkylene series polymer which has a reactive silicon group, a saturated hydrocarbon system polymer which has a reactive silicon group, an acrylic ester system copolymer which has a reactive silicon group (meta), and an organic polymer which blends two or more sorts chosen from a group, ** and others, can also be used.

[0108]

A manufacturing method of an organic polymer which blends a polyoxyalkylene series polymer which has a reactive silicon group, and an acrylic ester system copolymer which has a reactive silicon group (meta), Although proposed by JP,59-122541,A, JP,63-112642,A, JP,H6-172631,A, JP,H11-116783,A, etc., it is not limited to in particular these.

[0109]

It is known as compared with a case where a polyoxyalkylene series polymer is independently used for an organic polymer which blends a polyoxyalkylene series polymer which has this reactive silicon group, and an acrylic ester system copolymer which has a reactive silicon group (meta) that stability is bad. Then, the above-mentioned general formula (6) aa a polyoxyalkylene series polymer component in the aforementioned organic polymer to blend :

$-SiOR^4)_3$ (6)

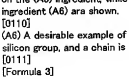
A polyoxyalkylene series polymer (A5) which has a basis expressed with (R^4 in a formula is the same as the above) is used, An organic polymer blended with an acrylic ester system copolymer (A6) which has a reactive silicon group (meta) has outstanding stability, endurance, and creep resistance based on the (A5) ingredient, while outstanding weatherability and an adhesive property based on an ingredient (A6) are shown.

[0110]

(A6) A desirable example of an acrylic ester (meta) system copolymer of an ingredient has a reactive silicon group, and a chain is a following general formula substantially (14). :

[0111]

[Formula 3]



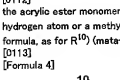
(1 4)

[0112]

the acrylic ester monomer unit which has an alkyl group of the carbon numbers 1-8 expressed with (a hydrogen atom or a methyl group, and R^{11} show the alkyl group of the carbon numbers 1-8 among a formula, as for R^{10}) (meta-), and following general formula (15):

[0113]

[Formula 4]



(1 5)

[0114]

(-- the inside of a formula, and R^{10} -- the above -- the same -- R^{12} shows a with a carbon numbers of ten or more alkyl group --) -- to a copolymer which consists of an acrylic ester monomer unit which has a with a carbon numbers of ten or more expressed alkyl group (meta-). It is the method of blending and manufacturing a polyoxyalkylene series polymer which has a reactive silicon group.

[0115]

as R^{11} of said general formula (14) -- the carbon numbers 1-8 of a methyl group, an ethyl group, a propyl group, n-butyl group, t-butyl group, a 2-ethylhexyl group, etc. -- desirable -- 1-4 -- an alkyl group of 1-2 is raised still more preferably. An alkyl group of R^{11} may be independent and may be mixed two or more sorts.

[0116]

as R^{12} of said general formula (15) -- ten or more carbon numbers of a lauryl group, a tridecyl group, a cetyl group, a stearyl group, a behenyl group, etc. -- usually -- 10-30 -- a long-chain alkyl group of 10-20 is raised preferably. Like a case of R^{11}, an alkyl group of R^{12} may be independent and may be mixed two or more sorts.

[0117]

Although a chain of a ** (meta) acrylic ester system copolymer consists of a monomeric unit of a formula (14) and a formula (15) substantially, a "real target" here means that the sum total of a monomeric unit of a formula (14) which exists in this copolymer, and a formula (15) surpasses 50 % of the weight. The sum total of a monomeric unit of a formula (14) and a formula (15) is 70 % of the weight or more preferably.

[0118]

As for an abundance ratio of a monomeric unit of a formula (14), and a monomeric unit of a formula (15), 95:5-40:60 are preferred at a weight ratio, and 90:10-60:40 are still more preferred.

[0119]

As monomeric units other than a formula (14) which may be contained in this copolymer, and a formula (15), For example, acrylic acid, such as acrylic acid and methacrylic acid; Acrylamide, Amide groups, such as methacrylamide, N-methylolacrylamide, and N-methylolmethacrylamide, Epoxy groups, such as glycidyl acrylate and glycidyl methacrylate, Diethylamino ethyl acrylate, diethylamino ethyl methacrylate, A monomer containing amino groups, such as aminoethyl vinyl ether; a monomeric unit which originates in acrylonitrile, styrene, alpha-methylstyrene, alkyl vinyl ether, VCM/PVC, vinyl acetate, vinyl propionate, ethylene, etc. in addition to this is raised.

[0120]

Although an organic polymer which blends a saturated hydrocarbon system system polymer which has a reactive silicon group, and an acrylic ester system copolymer which has a reactive silicon group (meta) is proposed by JP,H1-168764,A, JP,2000-186176,A, etc., It is not limited to in particular these.

[0121]

A method of polymerizing an acrylic ester (meta) system monomer elsewhere under existence of an organic polymer which has a reactive silicon group as a manufacturing method of an organic polymer which blends an acrylic ester system copolymer which has a reactant silicon functional group (meta) can be used. Although this manufacturing method is concretely indicated by each gazette, such as JP,59-78223,A, JP,59-168014,A, JP,60-228516,A, and JP,60-228517,A, it is not limited to these.

[0122]

In this invention, silicate can be used as a (B) ingredient. This silicate has the function to improve the stability of an organic polymer which is the (A) ingredient of this invention, endurance, and creep resistance.

[0123]

(B) Silicate which is an ingredient is a general formula (16).

$Si(OR^{13})_4$ (16)

the inside of a formula, and R^{13} -- respectively -- independent -- a hydrogen atom or an alkyl group of the carbon numbers 1-20. They are an aryl group of the carbon numbers 6-20, and the univalent hydrocarbon group chosen from an aralkyl group of the carbon numbers 7-20. They are tetra alkoxysilane expressed or its partial hydrolysis condensate.

[0124]

As an example of silicate, for example A tetramethoxy silane, a tetraethoxysilane, Ethoxy trimethoxysilane, dimethoxy diethoxysilane, methoxy triethoxysilane, Tetra alkoxysilane (tetraalkyl silicate), such as tetra n-propoxysilane, tetra i-propoxysilane, tetra n-butoxysilane, tetra i-butoxysilane, and tetra t-butoxysilane, and those partial hydrolysis condensates are raised.

[0125]

Since a partial hydrolysis condensate of tetra alkoxysilane has an improvement effect of the stability of this invention, endurance, and creep resistance larger than tetra alkoxysilane, it is preferred.

[0126]

A thing which was made to add and carry out partial hydrolysis of the water to tetra alkoxysilane by a usual method as a partial hydrolysis condensate of said tetra alkoxysilane for example, and was made to condense is raised. A commercial thing can be used for a partial hydrolysis condensate of an ORGANO silicate compound. As such a condensate, the methylsilicate 51, the ethyl silicate 40 (all are made in Col Coat), etc. are mentioned, for example.

[0127]

Silicate (B) shows an improvement effect of still better stability, endurance, and creep resistance by combining with an ingredient (A1) of this invention, an ingredient (A2), and the (A3) ingredient. By combining with an ingredient (A1) especially shows an improvement effect of good stability, endurance, and creep resistance.

[0128]

(B) As amount of ingredient used, 0.1 - 10 weight section is preferred to (A) ingredient 100 weight section, and also 1 - 5 weight section is preferred. (B) If loadings of an ingredient are less than this

range, an improvement effect of stability, endurance, and creep resistance may not be enough, and a cure rate may become slow if loadings of the (B) ingredient exceed this range. The above-mentioned silicate may be used only by one kind, and may carry out two or more kind mixing usa.

[0129]

In this invention, carboxylic acid tin salt can be used as a (C) ingredient. As compared with other silanol condensation catalysts, the stability of a hardened material obtained, endurance, and creep resistance can be improved by using this carboxylic acid tin salt as a silanol condensation catalyst of an organic polymer which is an ingredient (A1) of this invention.

[0130]

Limitation in particular does not have carboxylic acid tin salt (C) used for this invention, and various kinds of compounds can be used for it.

[0131]

As carboxylic acid which has an acid radical of carboxylic acid tin salt (C) here, a carboxylic acid group content compound of a hydrocarbon system of 2–40 is suitably used for a carbon number including carbonyl carbons, and carboxylic acid of a hydrocarbon system of the carbon numbers 2–20 may be especially used suitably from a point of availability.

[0132]

When it illustrates concretely, acetic acid, propionic acid, butanoic acid, a valeric acid, caproic acid, Enanthic acid, caprylic acid, 2-ethylhexanoic acid, pelargonic acid, capric acid, Undecanoic acid, lauric acid, trideoylacid, myristic acid, pentadecyl acid, Pulmitic acid, heptadecoylacid, stearic acid, nonadecanoic acid, arachin acid, Behenic acid, lignoceric acid, cerinic acid, montanic acid, melissic acid, Straight chain saturated fatty acid groups, such as RAKUSERU acid; Undecylenic acid, Linder acid, Tauzuic acid, FIZETERIN acid, myristeleic acid, 2-hexadecenoic acid, 6-hexadecenic acid, 7-hexadecenoic acid, palmitoleic acid, a petroselinic acid, Oleic acid, elaidic acid, ASUKUREPIN acid, vaccenic acid, gadoleic acid, Gondo Inn acid, a cetoleic acid, erucic acid, brassidic acid, selacholeic acid, KISHIMEN acid, RUMEKUEN acid, acrylic acid, methacrylic acid, angelic acid. Monoene unsaturated fatty acid, such as crotonic acid, isocrotonic acid, and 10-undecenoic acid; Reno elaidic acid, Linolic acid, 10,12-octadecadienoic acid, HIRAGO acid, alpha-eleostearic acid, beta-eleostearic acid, punicic acid, linolenic acid, 8 and 11, 14-eicosatrienoic acid, A 7,10,13-docosatrienoic acid, 4,8,11,14-hexadeca tetraenoic acid, MOROKUOHI acid, steer RIDON acid, arachidonic acid, 8, 12 and 16, 19-docosatetraenoic acid, 4,8,12,15,18-eicosapentaenoic acid, clupanodonic acid, herring acid, Polyene unsaturated fatty acid, such as docosahexaenoic acid; 1-methylbutyric acid, Isobutyric acid, 2-ethylbutanoic acid, isovaleric acid, tuberculostearic acid, Branch fatty acid, such as a pivalic acid and neo decanoic acid; PUROPI all acid, a tariric acid, Fatty acid with triple bonds, such as steer roll acid, a crepenynic acid, KISHIMENIN acid, and 7-hexa crepe-de-China acid; Naphthenic acid, A malvalic acid, sterculic acid, HIDONO carbyne acid, chaulmoogric acid, Alicyclic carvone acids, such as gorlic acid; Acetoacetic acid, ethoxyacetic acid, Glyoxylic acid, glycolic acid, glucoside acid, sabinic acid, 2-hydroxytetradecanoic acid, IPURORU acid, 2-hydroxyhexadecanoic acid, YARAPI Norian acid, uni-PERIN acid, AMBURETTORU acid, ARYURITTO acid, 2-hydroxyoctadecanoic acid, 12-hydroxyoctadecanoic acid, 18-hydroxyoctadecanoic acid, 9,10-dihydroxyoctadecanoic acid, Oxygenated fatty acid, such as recinoleic acid, cam RAREN acid, licanic acid, ferron acid, and cerebronic acid; a halogenation object of monocarboxylic acid, such as chloracetic acid, 2-chloroacrylic acid, and chlorobenzoic acid, etc. are mentioned. As aliphatic dicarboxylic acid, adipic acid, azelaic acid, pimelic acid. Saturation dicarboxylic acid, such as SUPERIN acid, sebacic acid, ethylmalonic acid, glutaric acid, oxalic acid, malonic acid, succinic acid, and oxydiacetic acid; unsaturated dicarboxylic acid, such as maleic acid, fumaric acid, acetylene dicarboxylic acid, and itaconic acid, etc. are mentioned. As aliphatic polycarboxylic acid, tricarboxylic acid, such as aconitic acid, citrate, and isocitric acid, etc. are mentioned. As aromatic carboxylic acid, benzoic acid, 9-anthracene carboxylic acid. Aromatic monocarboxylic acids, such as atrolactinic acid, anisic acid, isopropylbenzoic acid, salicylic acid, and toluic acid; aromatic polycarboxylic acids, such as phthalic acid, isophthalic acid, terephthalic acid, carboxyphenyl acetic acid, and pyromellitic acid, etc. are mentioned. In addition, amino acid, such as an alanine, leucine, threonine, aspartic acid, glutamic acid, arginine, cystein, methionine, phenylalanine, tryptophan, and histidine, is mentioned.

[0133]

Especially acquisition is easy, and is cheap and a point that compatibility with an ingredient (A1) is

good to said carboxylic acid has 2-ethylhexanoic acid, octylic acid, neo decanoic acid, oleic acid, or preferred naphthenic acid.

[0134]

when the melting point of said carboxylic acid is high (crystallinity is high), the melting point becomas high in a similar manner, and it is hard to deal with carboxylic acid tin salt which has the acid radical (workability — bad). Therefore, as for the melting point of said carboxylic acid, it is preferred that it is 65 ** or less, it is more preferred that it is −50–50 **, and it is preferred that it is especially −40–35 **.

[0135]

when a carbon number of said carboxylic acid is large (a molecular weight is large), it becomes liquefied and carboxylic acid tin salt which has the acid radical becomes a thing which has a high solid state or viscosity and which is hard to deal with it (workability — bad). On the contrary, when a carbon number of said carboxylic acid is small (a molecular weight is small), catalyst ability of carboxylic acid metal salt may fall [carboxylic acid tin salt which has the acid radical], including mostly an ingredient which volatilizes easily with heating. Especially on conditions (thin layer) which extended a constituent thinly, volatilization by heating may be large and catalyst ability of carboxylic acid metal salt may fall greatly. Therefore, as for said carboxylic acid, it is preferred that carbon numbers including carbon of a carbonyl group are 2–20, it is more preferred that it is 6–17, and it is preferred that it is especially 8–12.

[0136]

It is preferred that it is the tin salt of a point of the ease (workability, viscosity) of dealing with it of carboxylic acid tin salt to dicarboxylic acid or monocarboxylic acid, and it is more preferred that it is the tin salt of monocarboxylic acid.

[0137]

As said monocarboxylic acid tin salt, it is a general formula (17). :

$Sn(OCOR)_2$ (17)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.) Two RCOO-bases may be the same and may differ. A divalent Sn compound expressed or general formula (18) :

$Sn(OCOR)_4$ (18)

(It is the same as the above the inside R of a formula.) Two RCOO-bases may be the same and may differ. A tetravalent Sn compound expressed is preferred. A divalent Sn compound expressed with a general formula (17) from a point of hardenability and availability is more preferred.

[0138]

carboxylic acid tin salt (neo decanoic acid tin,) in which said carboxylic acid tin salt (C) is carboxylic acid tin salt (2-ethylhexanoic acid tin etc.) and the 4th class carbon whose carbon of an alpha position of a carboxyl group is the 3rd class carbon Pivalio-acid tin etc. are more preferred from a cure rate being quick, and especially carboxylic acid tin salt whose carbon atom which adjoins a carbonyl group is the 4th class carbon is preferred.

[0139]

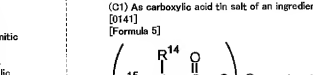
Especially in this invention, carbon of an alpha position of a carboxyl group uses carboxylic acid tin salt which is the 4th class carbon as an ingredient (C1) in carboxylic acid tin salt (C).

[0140]

(C1) As carboxylic acid tin salt of an ingredient, it is a general formula (19). :

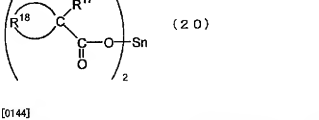
[0141]

[Formula 5]



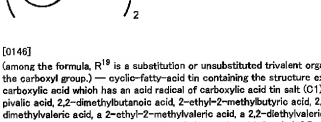
(19)

[0142]
(among the formula, R^{14}, R^{15}, and R^{16} are the independent substitution or unsubstituted univalent organic groups, respectively, and may contain the carboxyl group.) — the chain fatty acid tin expressed or general formula (20):
[0143]
[Formula 6]



(20)

[0144]
(among the formula, an organic group univalent [substitution or unsubstituted] in R^{17} and R^{18} are substitution or unsubstituted divalent organic groups, and the carboxyl group may be included, respectively.) — and general formula (21):
[0145]
[Formula 7]



(21)

[0146]
(among the formula, R^{19} is a substitution or unsubstituted trivalent organic group, and may contain the carboxyl group.) — cyclic-fatty-acid tin containing the structure expressed is mentioned. If the carboxylic acid whioh has an acid radical of carboxylic acid tin salt (C1) is illustrated concretely, A pivalic acid, 2,2-dimethylbutanoic acid, 2-ethyl-2-methylbutyric acid, 2,2-diethylbutanoic acid, A 2,2-dimethylvaleric acid, a 2-ethyl-2-methylvaleric acid, a 2,2-diethylvaleric acid, 2,2-dimethylhexana acid, 2,2-diethylhexanoic acid, 2,2-dimethyloctanoic acid, 2-ethyl-2,5-dimethylhexane acid, neo decanoic acid, BASA tic acid. Chain monocarboxylic acid, such as 2,2-dimathyl- 3-hydroxypropionic acid. Dimethylmalonic acid, ethyl methylmalonic acid, diethylmalonic acid, 2,2-dimethyl amber acid, Chain dicarboxylic acid, such as 2,2-diethyl amber acid and 2,2-dimethylglutaric acid, Chain tricarboxylic acid, such as 3-methyliso citrate and 4,4-dimethylaconitic acid, 1-methylcyclopentanecarboxylic acid, 1,2,2-trimethyl 1,3-cyclopentane dicarboxylic acid, 1-methylcyclohexane carboxylic acid, 2-methylbicyclo[2.2.1]-5- heptene-2-carboxylic acid, 2-methyl-7-oxabicyclo [2.2.1]-5-heptene-2-carboxylic acid, 1-adamantane carboxylic acid, Annular carboxylic acid, such as bicyclo[2.2.1] heptane- 1-carboxylic acid and bicyclo[2.2.2] octane- 1-carboxylic acid, etc. are mentioned. These can also be used although many compounds containing such a structure to a natural product exist.
[0147]
From a point that compatibility with an ingredient and workability are especially (A1) good, tin monocarboxylate is more preferred and also chain tin monocarboxylate is more preferred. Since acquisition is easy, pivalic-acid tin, neo decanoic acid tin, BASA tic acid tin, 2,2-dimethyloctanoic acid tin, especially 2-ethyl-2,5-dimethylhexane acid tin, etc. are preferred.
[0148]
(C1) Also in an ingredient, although carboxylata of divalent tin and carboxylate of tetravalent tin are mentioned like a case of the above-mentioned (C) ingredient, carboxylate of a point of hardenability

and availability to divalent tin is more preferred.
[0149]
As for a carbon number of carboxylic acid which has an acid radical of an ingradient (C1), it is preferred that it is 5-20, it is more preferred that it is 6-17, and it is preferred that it is especially 8-12. Since compatibility with an ingredient may fall that it is easy to become a solid state (A1) and catalytic activity may fall if a carbon number increases more than this range, it is not desirable. It is not desirable from on the other hand, volatility, the increasa of a smell, and the thin layer hardenability of a hardenability constituent falling, if there are few carbon numbers.
[0150]
As an ingredient, from these points (C1) Neo decanoic acid tin (divalent), BASA tic acid tin (divalent), 2,2-dimethyloctanoic acid tin (divalent), 2-ethyl-2,5-dimethylhexane acid tin (divalent), Neo decanoic acid tin (tetravalence), BASA tic acid tin (tetravalence), 2,2-dimethyloctanoic acid tin (tetravalence), and especially 2-ethyl-2,5-dimethylhexane acid tin (tetravalence) are preferred.
[0151]
(C) As amount of an ingredient and (C1) ingredient used, about 0.01-20 weight sections are preferred to ingredient (A1) 100 weight section, and also about 0.5-10 weight sections are preferred. Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings are less than this range, it is not desirable. On the other hand, if loadings exceed this range, working life becomes short too much, and workability may worsen, and it is not desirable from a point of storage stability.
[0152]
The (C) ingredient and (C1) an ingredient can be used combining two or more sorts besides using it alone.
[0153]
On the other hand, only of the (C) ingredient and (C1) an ingredient, activity is low, and when moderate hardenability is not acquired, an amine compound can be added as a co-catalyst.
[0154]
As various amine compounds, although indicated to JP,H5-287187,A, for example, Specifically Methylamine, ethylamine, propylamine, isopropylamine, A butylamine, amyl amine, hexylamine, octylamine, 2-ethylhexylamine, Nonyl amine, decyl amine, lauryl amine, pentadecyl amine, Aliphatic series primary amines, such as Sept lles amine, stearylamine, and cyclohexylamine; Dimethylamine, Diethylamine, dipropyl amine, diisopropylamine, dibutyl amine, Diamylamine, dioctyl amine, di(2-ethylhexyl) amine, Didecyl amine, dilauryl amine, JISECHIRU amine, distearyl amine, Aliphatic series secondary amines, such as methylstearylamine, ethylstearylamine, and butylstearylamine; Triethylamine, Aliphatic series tertiary amines, such as triamylamine, trihexyl amine, and trioctylamine; Triaryl amina, Aliphatic series unsaturation amines, such as oleylamine; aromatic-amine; Lauryl aniline, stearylaniline, a triphenylamine, N,N-dimethylaniline, dimethylbenzyl aniline, etc. reach, As other amines, monoethanolamine, diethanolamine, Triethanolamine, dimethylamino ethanol, diethylenetriamine, Triethylenetetramine, tetraethylenepentamine, benzylamine, Diethylamino propylamine, xylylena diamine, ethylenediamine, Hexamethylenediamine, dodecamethylenediamine, dimethylethylenediamine, Triethylenediamine, guanidine, diphenylguanidine, N,N,N', and N''-tetramethyl 1,3-butanediamine, N,N,N', N''-tetramethyl ethylene diamine, 2,4,6-tris(dimethyl aminomethyl) phenol, Although morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo (5, 4, 0) undecene 7 (DBU) etc. are mentioned, it is not limited to these.
[0155]
As for loadings of said amine compound, about 0.01-20 weight sections are preferred to organic polymer 100 weight section of an ingredient (A1), and also its 0.1 to 5 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 20 weight sections, pot life may become short too much and is not preferred from a point of workability.
[0156]
In this invention, an organic tin catalyst can be used as a (D) ingredient. When this organic tin catalyst is used as a silanol condensation catalyst of an organic polymer which has a reactive silicon group, as compared with other silanol condensation catalysts, a hardenability constituent with high

catalytic activity, and good depths hardenability and an adhesive property is obtained. However, according to an addition of this organic tin catalyst, the stability of a hardened material of a hardenability constituent obtained, endurance, and creep resistance fall.

[0157]

A hardenability constituent which addad an organic tin catalyst of the (D) ingradient by using an organic polymer which is an ingredient (A1) of this invention as a polymar component, Catalytic activity is high, and depths hardenability and an adhesive property are good, and the stability of a hardened material obtained, endurance, and creep resistance can be maintained highly.

[0158]

In using adhesives or a sealing material which, on the other hand, contains an organic polymer which has a reactive silicon group as the main ingredients for a use which needs endurance, it uses carboxylic acid tin salt of the aforementioned (C) ingredient as a curing catalyst in many cases. however, if this carboxylic acid tin salt is used as a curing catalyst, when it will be alike around a masonry joint and a sealing material will remain by a thin layer, it is hard to harden that thin layer portion, and may remain on conditions of heat and high humidity especially with un-hardening. On the other hand, if said organic tin catalyst (D) is used as a curing catalyst, as mentioned above, stability and endurance will fall, but the hardenability of a thin layer part is good. Then, if an organic tin catalyst of an organic polymer and the (D) ingredient which is an ingredient (A1) of this invention is combined, the hardenability of a thin layar part can be improved notably, maintaining the stability of a hardened material obtained, and endurance highly.

[0159]

However, even if it combines with an organic polymer which is an ingredient (A1) of this invention, depending on an addition of an organic tin catalyst of the (D) ingredient, stability and endurance may fall a little. Then, it is more preferred to decrease the quantity of an addition of the (D) ingredient to such an extent that carboxylic acid tin salt of the (C) ingredient is used together and sufficient hardenability, depths hardenability, an adhesive property, and thin layer hardenability are acquired with an organic tin catalyst of the (D) ingredient as a curing catalyst.

[0160]

As an example of said organic tin catalyst (D), they are dialkyl tin carboxylate, dialkyl tin oxide, and a general formula (22). :

$Q_gSn(OZ)_{4-g}$ or $[Q_gSn(OZ)]_2O$ (22)

(Z expresses among a formula an organic group which has a functional group with which Q can form a coordinate bond in an inside of a univalent hydrocarbon group of the carbon numbers 1-20, or self for a univalent hydrocarbon group of the carbon numbers 1-20 to Sn.) g is 0, 1, 2, or 3. A compound etc. which are shown as shown. Tetravalent tin compounds, such as dialkyl tin oxide and dialkyl tin diacetate, It is usable as a (D) ingredient also in a reactant with a low molecule silicon compound which has hydrolytic silicon groups, such as a tetraethoxysilane, methyl triethoxysilana, diphanyldimathoxysilane, and phenyltrimethoxysilana. Since activity as a silanol condensation catalyst is high, chelate compound and tin alcoholates, such as a compound shown by a general formula (22) also in these, i.e., dibutyl tin bisacetylacetonate etc., are more preferred.

[0161]

As an example of said dialkyl tin carboxylate. For example, dibutyltin dilaurate, dibutyltin diacetate, a dibutyl tin diethylhexano rate, Dibutyl tin JIOKUTETO, dibutyl tin dimethylmalate, dibutyl tin diethyl malate, Dibutyl tin dibutyl maleate, dibutyl tin diisooctyl malate, Dibutyl tin ditridecyl malate, dibutyl tin dibenzyl malate, dibutyltin maleate, dioctyl tin diacetate, dioctyl tin distearate, dioctyl tin dilaurate, dioctyl tin diethyl malate, dioctyl tin diisooctyl malate, etc. are mentioned.

[0162]

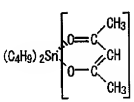
As an example of said dialkyl tin oxide, dibutyl tin oxide, dioctyl tin oxide, a mixture of dibutyl tin oxide and phthalic ester, etc. are mentioned.

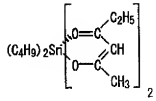
[0163]

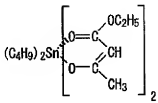
If said chelate compound is illustrated concretely,

[0164]

[Formula 8]







[0165]

Although ** is mentioned, it is not limited to these. In these, its catalytic activity is high, and it is low cost, and since dibutyl tin bisacetylacetonate is easy to receive, it is the most preferred.

[0166]

If said tin alcoholates are illustrated concretely,

[0167]

[Formula 9]

$(C_4H_9)_3SnOCH_3$

$(C_4H_9)_2Sn(OCH_3)_2$

$C_4H_9Sn(OCH_3)_3$

$Sn(OCH_3)_4$

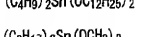
$(C_4H_9)_2Sn(OC_3H_7)_2$

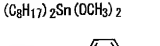
$(C_4H_9)_2Sn(OC_4H_9)_2$

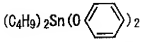
$(C_4H_9)_2Sn(OC_8H_{17})_2$

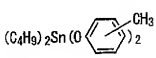
$(C_4H_9)_2Sn(OC_{12}H_{25})_2$

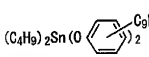
$(C_8H_{17})_2Sn(OCH_3)_2$











[0168]
Although ** is mentioned, it is not limited to these. In these, a dialkyl tin JIARUKOKI side is preferred. Especially the dibutyl tin JIMETOKI side is low cost, and since it is easy to receive, it is

preferred.
[0169]
(D) As amount of ingredient used, about 0.01–20 weight sections are preferred to ingredient (A1) 100 weight section, and also about 0.1–10 weight sections are preferrad. Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings are less than this range, it is not desirable. On the other hand, if loadings exceed this range, working life becomes short too much, and workability may worsen, and it is not desirable from a point of storage stability.
[0170]
As amount of [in case used of using the (D) ingredient and the (C) ingredient together as a curing catalyst], (A1) It is preferred to consider it as (C) ingredient:0.5 – 20 weight section and (D) ingredient:0.01 – 10 weight section to ingredient 100 weight section, and also it is more preferred to consider it as (C) ingredient:1 – 10 weight section and (D) ingredient:0.02 – 5 weight section. (C) When loadings of an ingredient are less than this range, a cure rate may become slow, when loadings exceed this range, working life becomes short too much and workability may worsen. (D) The stability of a hardened material which will be obtained if an improvement effect of hardenability, depths hardenability, an adhesive property, and thin layer hardenability may not be enough if loadings of an ingredient are less than this range, and loadings exceed this range, endurance, and creep resistance may worsan.
[0171]
The (D) ingredient can be used combining two or more sorts besides using it alone.
[0172]
In this invention, a non-tin catalyst can be used as a (E) ingradient. This non-tin catalyst has a function which improvas the stability of a hardened material obtained, endurance, and creep resistance as compared with other silanol condensation catalysts, when it uses as a silanol condensation catalyst of an organic polymer which is an ingredient (A1) of this invention. A non-tin catalyst which is the (E) ingredient is an eco-friendly curing catalyst with high social needs.
[0173]
As a non-tin catalyst which is the (E) ingredient which can be used for this invention, although there is no restriction in particular, an organic metallic compound containing carboxylic acid, carboxylic acid metal salt other than carboxylic acid tin salt, organic sulfonic acid, alkyl acid phosphate and 3B fellows, and 4A group metal, etc. are illustrated.
[0174]
The various above-mentioned carboxylic acid which has an acid radical of carboxylic acid tin salt which is the (C) ingredient as carboxylic acid can be illustrated.
[0175]
As for said carboxylic acid, it is preferred like carboxylic acid tin salt (C) that carbon numbers including carbon of a carbonyl group are 2–20, it is more preferred that it is 6–17, and it is preferred that it is especially 8–12. A point to dicarboxylic acid or monocarboxylic acid of the ease (workability, viscosity) of dealing with it of carboxylic acid is preferred, and monocarboxylic acid is more preferred. carboxylic acid (neo decanoic acid.) in which said carboxylic acid is carboxylic acid (2-ethylhexanoic acid etc.) and the 4th class carbon whose carbon of an alpha position of a carboxyl group is the 3rd class carbon A pivalic acid etc. are more preferred from a cure rate being quick, and especially carboxylic acid whose carbon atom which adjoins a carbonyl group is the 4th class carbon is preferred.
[0176]
Especially as carboxylic acid, 2-ethylhexanoic acid, neo decanoic acid, BASA tic acid, 2,2-dimethyloctanoic acid, and 2-ethyl-2,5-dimethylhexane acid are preferred from a point of availability, hardenability, and workability.
[0177]
As carboxylic acid metal salt other than said carboxylic acid tin salt, metal salt of the various above-mentioned carboxylic acid can be used conveniently.
[0178]
In carboxylic acid metal salt other than said carboxylic acid tin salt, carboxylic acid bismuth, Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, Carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel,

carboxylic acid cobalt, a carboxylic acid zirconium, and carboxylic acid cerium. From a high point, the activity of a catalyst is preferred and Carboxylic acid bismuth, carboxylic acid calcium, Carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid potassium, Carboxylic acid barium, carboxylic acid manganese, and a carboxylic acid zirconium are more preferred, Carboxylic acid bismuth, carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, and a carboxylic acid zirconium are still more preferred, and carboxylic acid bismuth, carboxylic acid iron, and carboxylic acid titanium are especially the most preferred.
[0179]
Carboxylic acid bismuth, carboxylic acid calcium, carboxylic acid vanadium, Carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium, It is more desirable from a point with little coloring of a hardenability constituent obtained, and a point that the heat resistance of a hardened material and weatherability which are obtained are high, and carboxylic acid bismuth, carboxylic acid calcium, carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium, and a carboxylic acid zirconium are still more preferred.
[0180]
It is more preferred that it is metal salt of a point of the ease (workability, viscosity) of dealing with it of carboxylic acid metal salt to monocarboxylic acid.
[0181]
As said monocarboxylic acid metal salt, it is general formula (23) – (35). :
Bi(OCOR) $_3$ (23)
Ca(OCOR) $_2$ (24)
V(OCOR) $_3$ (25)
Fe(OCOR) $_2$ (26)
Fe(OCOR) $_3$ (27)
Ti(OCOR) $_4$ (28)
K(OCOR) (29)
Ba(OCOR) $_2$ (30)
Mn(OCOR) $_2$ (31)
nickel(OCOR) $_2$ (32)
Co(OCOR) $_2$ (33)
Zr(O) (OCOR) $_2$ (34)
Ce(OCOR) $_3$ (35)
(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.) Two RCOO-bases may be the same and may differ. Carboxylic acid metal salt expressed is preferred.
[0182]
As a carboxylic acid group of carboxylic acid metal salt other than said carboxylic acid tin salt, an acid radical of various carboxylic acid tin salt illustrated as the aforementioned (C) ingredient can be mentioned.
[0183]
From a viewpoint of the availability of a raw material, and compatibility, as an example of desirable carboxylic acid metal salt, 2-ethylhexanoic acid bismuth (trivalent), 2-ethylhexanoic acid iron (divalent), 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid titanium (tetravalence), 2-ethylhexanoic acid vanadium (trivalent), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid manganese (divalent), 2-ethylhexanoic acid nickel (divalent), 2-ethylhexanoic acid cobalt (divalent), 2-ethylhexanoic acid zirconium (tetravalence), 2-ethylhexanoic acid cerium (trivalent), neo decanoic acid bismuth (trivalent), Neo decanoic acid iron (divalent), neo decanoic acid iron (trivalent), neo decanoic acid titanium (tetravalence), Neo decanoic acid vanadium (trivalent), neo decanoic acid calcium (divalent), Neo decanoic acid potassium (univalent), neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence), Neo decanoic acid cerium (trivalent), bismuth oleate

(trivalent), oleic acid iron (divalent), oleic acid iron (trivalent), oleic acid titanium (tetravalence), oleic acid vanadium (trivalent), Oleic acid calcium (divalent), oleic acid potassium (univalent), oleic acid barium (divalent), Manganese oleate (divalent), oleic acid nickel (divalent), oleic acid cobalt (divalent), An oleic acid zirconium (tetravalence), oleic acid cerium (trivalent), naphthenic acid bismuth (trivalent), Naphthenic acid iron (divalent), naphthenic acid iron (trivalent), naphthenic acid titanium (tetravalence), Naphthenic acid vanadium (trivalent), calcium naphthenate (divalent), naphthenic acid potassium (univalent), Naphthenic acid barium (divalent), manganese naphthenate (divalent), naphthenic acid nickel (divalent), cobalt naphthenate (divalent), a naphthenic acid zirconium (tetravalence), naphthenic acid cerium (trivalent), etc. are mentioned.
[0184]
2-ethylhexanoic acid bismuth (trivalent) from a viewpoint of catalytic activity, 2-ethylhexanoic acid iron (divalent), 2-ethylhexanoic acid iron (trivalent), 2-ethylhexanoic acid titanium (tetravalence), Neo decanoic acid bismuth (trivalent), neo decanoic acid iron (divalent), neo decanoic acid iron (trivalent), Neo decanoic acid titanium (tetravalence), bismuth oleate (trivalent), oleic acid iron (divalent), Oleic acid iron (trivalent), oleic acid titanium (tetravalence), naphthenic acid bismuth (trivalent), Naphthenic acid iron (divalent), naphthenic acid iron (trivalent), and naphthenic acid titanium (tetravalence) are more preferred, and 2-ethylhexanoic acid iron (trivalent), neo decanoic acid iron (trivalent), and especially naphthenic acid iron (trivalent) are preferred.
[0185]
2-ethylhexanoic acid bismuth (trivalent) from a viewpoint of coloring, 2-ethylhexanoic acid titanium (tetravalence), 2-ethylhexanoic acid calcium (divalent), 2-ethylhexanoic acid potassium (univalent), 2-ethylhexanoic acid barium (divalent), 2-ethylhexanoic acid zirconium (tetravalence), Neo decanoic acid bismuth (trivalent), neo decanoic acid titanium (tetravalence), Neo decanoic acid calcium (divalent), neo decanoic acid potassium (univalent), Neo decanoic acid barium (divalent), a neo decanoic acid zirconium (tetravalence), Bismuth oleate (trivalent), oleic acid titanium (tetravalence), oleic acid calcium (divalent), Oleic acid potassium (univalent), oleic acid barium (divalent), an oleic acid zirconium (tetravalence), Naphthenic acid bismuth (trivalent), naphthenic acid titanium (tetravalence), calcium naphthenate (divalent), naphthenic acid potassium (univalent), naphthenic acid barium (divalent), and a naphthenic acid zirconium (tetravalence) are more preferred.
[0186]
Toluenesulfonic acid, styrene sulfonic acid, etc. are raised as organic sulfonic acid.
[0187]
Alkyl acid phosphate is -O-P (=O) OH. It is phosphoric ester containing a portion and alkyl acid phosphate as shown below is contained. An organic acid nature phosphoric ester compound is preferred in respect of compatibility and curing catalyst activity.
[0188]
An organic acid natura phosphoric ester compound is expressed with $_h(R^{20}-O)-P(=O)(-OH)_{3-h}$ (in the inside h of a formula, 1 or 2, and R^{20} show an organic residue).
[0189]
Below, it illustrates concretely.
$(CH_3O)_2$-P (=O) (-OH), (CH_3O)-P(=O) (-OH) $_2$, $(C_2H_5O)_2$-P (=O) (-OH), (C_2H_5O)-P(=O) (-OH) $_2$ and $_2(C_2H_5O)$-P (=O) (-OH), (C_3H_7O)-P(=O) (-OH) $_2$ and $_2(C_4H_9O)$-P (=O) (-OH), (C_4H_9O)-P(=O) (-OH) $_2$ and $_2(C_8H_{17}O)$-P (=O) (-OH), $(C_8H_{17}O)$-P(=O) (-OH) $_2$, $(C_{10}H_{21}O)_2$-P (=O) (-OH), $(C_{10}H_{21}O)$-P(=O) (-OH) $_2$, $(C_{18}H_{37}O)_2$-P (=O) (-OH), $(C_{18}H_{37}O)$-P(=O) (-OH) $_2$ and $_2(C_{16}H_{33}O)$-P (=O) (-OH), $(C_{16}H_{33}O)$-P(=O) (-OH) $_2$, $(HO-C_6H_{12}O)_2$-P (=O) (-OH), $(HO-C_6H_{12}O)$-P(=O) (-OH) $_2$, $(HO-C_8H_{16}O)$-P (=O) (-OH), $(HO-C_8H_{16}O)$-P(=O) (-OH) $_2$, [(CH$_2$ OH) (CHOH) O] $_2$-P (=O) (-OH), [(CH$_2$ OH) (CHOH) O]-P(=O) (-OH) $_2$, Although [(CH$_2$ OH) (CHOH) C$_2$H$_4$O] $_2$-P (=O) (-OH) and [(CH$_2$ OH) (CHOH) C$_2$H$_4$O]-P(=O) (-OH) $_2$ etc. are raised, it is not limited to the above-mentioned illustration substance.
[0190]
By carboxylic acid, carboxylic acid metal salt other than carboxylic acid tin salt, organic sulfonic acid, and alkyl acid phosphate, activity is low, and when moderate hardenability is not acquired, an amine

compound can be added as a co-catalyst.
[0191]
As various amine compounds, the indicated various above-mentioned amine compounds can be used as a co-catalyst of carboxylic acid tin salt (C).
[0192]
As for loadings of said amine compound, about 0.01-20 weight sections are preferred to organic polymer 100 weight section of an ingredient (A1), and also its 0.1 to 5 weight section is more preferred. A cure rate may become it slow that loadings of an amine compound are less than 0.01 weight sections, and a hardening reaction becomes fully difficult to advance. On the other hand, if loadings of an amine compound exceed 20 weight sections, pot life may become short too much and is not preferred from a point of workability.
[0193]
As a metal system compound of non-tin, besides carboxylic acid metal salt other than said carboxylic acid tin salt, An organic metallic compound containing 3B fellows and 4A group metal is raised, and although a titanate organic compound, an organoaluminium compound, an organic zirconium compound, an organic boron compound, etc. are preferred from a point of activity, it is not limited to these.
[0194]
As said titanate organic compound, tetraisopropyl titanate, Tetrabuthyl titanate, tetramethyl titanate, tetra (2-ethylhexyl titanate), Chelate compound, such as titanium chelate, such as titanium alkoxides, such as triethanolamine titanate, titanium tetra acetylacetonato, titanium ethylacetoacetate, octylane glycolate, and titanium lactate, etc. are raised.
[0195]
As said organoaluminium compound, aluminum isopropylate, Aluminum alkoxides, such as mono sec-butoxy aluminum diisopropylate and aluminum sec-butyrate. Aluminum chelate, such as aluminum tris acetylacetonato, aluminumtrisethylacetoacetate, and diisopropoxy aluminum ethylacetoacetate, is raised.
[0196]
As said zirconium compound, zirconium tetra isopropanal POKISAIDO, Zirconium alkoxides, such as a zirconium tetra-n PUROPI rate and zirconium normal butyrate. Zirconium chelate, such as zirconium tetra acetylacetonato, zirconium monoacetyl acetonate, zirconium bisacetylacetonate, zirconium acetylacetonato bis-ethylacetoacetate, and zirconium acetate, is raised.
[0197]
Although **** concomitant use is also possible so, these titanate organic compounds, an organoaluminium compound, an organic zirconium compound, an organic boron compound, etc., It is desirable in a viewpoint which can reduce the amount of catalyst used especially according to concomitant use with said amine compound or an alkyl-acid-phosphate compound since it is possible to improve activity, and more desirable in a viewpoint of adjustment of working life in hardenability and ordinary temperature in an elevated temperature.
[0198]
(E) As amount of ingredient used, about 0.01-20 weight sections are preferred to ingredient (A1) 100 weight section, and also about 0.5-10 weight sections are preferred. Since a cure rate may become slow and a hardening reaction will become fully difficult to advance if loadings are less than this range, it is not desirable. On the other hand, if loadings exceed this range, working life becomes short too much, and workability may worsen, and it is not desirable from a point of storage stability.
[0199]
The (E) ingredient can be used combining two or more sorts besides using it alone.
[0200]
In this invention, a minute hollow body can be used as a (F) ingredient. While improving the workability (********, thixotropy) of a constituent notably as indicated to JP,H11-35923,A or JP,H11-310772,A if this minute hollow body is used, it is known that a weight saving of a constituent and low-cost-izing are possible. However, it is known that the stability of a hardened material of a hardenability constituent and endurance which are obtained will fall according to an addition of this minuta hollow body.
[0201]

The hardenability constituent which added a minute hollow body of the (F) ingredient by using an organic polymer which is an ingredient (A1) of this invention as a polymer component can maintain highly the stability of a hardened material and endurance which are obtained, improving workability (********) notably.
[0202]
a very small hollow body (henceforth a balloon) which is the (F) ingredient of this invention is a hollow body by which a diameter was preferably constituted from material of minerals of 500 micrometers or less or stability of organicity 1 mm or less as indicated, for example on "state-of-the-art art of a functional filler" (CMC). (F) An ingredient in particular is not limited but it is [ingredient] usable in various kinds of publicly known balloons.
[0203]
As for average particle density of a balloon, it is preferred that it is 0.01 - 1.0 g/cm^3, it is more preferred that it is 0.03 - 0.7 g/cm^3, and it is preferred that it is especially 0.1 - 0.5 g/cm^3. If tensile strength of a hardened material may fall if average particle density is less than this range, and average particle density exceeds this range on the other hand, a workability improvement effect may not be enough.
[0204]
An inorganic system balloon is more preferred than a point of stability and endurance to an organic system balloon.
[0205]
As said inorganic system balloon, can illustrate a silicic acid system balloon and a non-silicic acid system balloon, and on a silicic acid system balloon. A milt balloon, perlite, glass balloons, a silica balloon, fly ash balloons, etc. can illustrate an alumina balloon, a zirconia balloon, a carbon balloon, etc. on a non-silicic acid system balloon. As an example of these inorganic system balloons, as a milt balloon, a win light by UCHI Chemicals, As a SANKI light by Sanki Engineering Co., Ltd., and glass balloons, KARUN by Nippon Sheet Glass Co., Ltd., The Sumitomo 3M cell star Z-28, MICRO BALLOON made from EMERSON&CUMING, CELAMIC GLASSMODULES made from PITTSBURGE CORNING, As GLASS BUBBLES made from 3M, FUJIBA lune made from Fuji SHIRISHIA Chemicals, and a silica balloon, as Q-CEL by Asahi Glass Co., Ltd., SAIRISHIA made from Fuji SHIRISHIA Chemicals, and fly ash balloons, CEROSPHERES made from PFAMARKETING, FILLITE made from FILLITE U.S.A, As an alumina balloon, as SW by Showa Denko K.K., and a zirconia balloon HOLLOW ZIRCONIUM SPHEES made from ZIRCOA, KUREKASU fair made from Kureha Chemicals and product car boss fair made from GENERAL TECHNOLOGIES are marketed as a carbon balloon.
[0206]
A balloon of thermosetting resin and a balloon of thermoplastics can be illustrated as said organic system balloon, On a thermosatting balloon, a phenol balloon, an epoxy balloon, and a urea balloon can illustrate a saran balloon, a polystyrene balloon, a polymathacrylate balloon, a polyvinyl alcohol balloon, and a styrene acrylic balloon at a thermoplastic balloon. A balloon of thermoplastics which constructed the bridge can also be used. A balloon after foaming may be sufficient, and a balloon here is made to foam, after blending a thing containing a foaming agent, and is good also as a balloon.
[0207]
As an example of these organic system balloons, as a phenol balloon, Union Carbide UCAR and PHENOLIC MICROBALLOONS, As an epoxy balloon, ECCOSPHERES made from EMERSON&CUMING, As a urea balloon, ECCOSPHERES VF-O made from EMERSON&CUMING, As a saran balloon, SARAN MICROSPHERES made from DOW CHEMICAL, Expancel made from Japanese Filament, the Matsumoto Yushi-Seiyaku Matsumoto microsphere, As a polystyrene balloon, DYLITE EXPANDABLE POLYSTYRENE made from ARCO POLYMERS, SX563 by Japan Synthetic Rubber Co., Ltd. (P) are marketed by EXPANDABLE POLYSTYRENE BEADS made from BASF WYANDOTE, and constructed type styrene acrylic acid balloon of a bridge.
[0208]
The above-mentioned balloon may be used alone, and two or more kinds may be mixed and it may be used. The surface of these balloons Fatty acid, fatty acid ester, rosin, What was processed in order to improve disparsibility and the workability of a compound by rosin acid lignin, a silane coupling agent, titanium coupling agent, aluminum cup ring agent, a polypropylene glycol, etc. can be used. Without spoiling pliability, and elongation and intensity among physical properties at the time of

stiffaning a compound, these balloons are used in order to carry out a weight saving and to cut down the cost.
[0209]
As for the amount of balloon used, about 0.1-50 weight sections are preferred to ingredient (A1) 100 weight section, and also its about 0.5-30 weight sections are preferred. When a workability improvement effect may not be enough if loadings are less than this range, and loadings exceed this range, tensile strength of a hardened material may fall or stability and endurance may worsen.
[0210]
At this invention, it is a general formula as a (G) ingredient (7). :
$-SiR^5_c(OR^6)_{3-c}$ (7)
(Among a formula, c R^5 is the organic groups of monovalence of the carbon numbers 1-20 independently, and 3-c R^6, respectively) It is an organic group of monovalence of the carbon numbers 2-20 independently, and c shows 0, 1, or 2, respectively. An aminosilane coupling agent which has a basis expressed can be used. General formula (6) which is the (A4) ingredient of this invention about this (G) ingredient :
$-Si(OR^4)_3$ (6)
While having stability, endurance, and creep resistance outstanding by adding to an organic polymer which has a basis expressed with (R^4 in a formula is the same as the above), it becomes a hardenability constituent in which an outstanding adhesive property is shown. To a reactive silicon group of this (G) ingredient. Even if an ester exchange reaction between reactive silicon groups of the (G) ingredient and the (A4) ingredient advances after mixing with the (A4) ingredient since it does not have a methoxy group as an alkoxy group combined with a silicon atom, a reactant high methoxy silyl group does not generate to a reactive silicon group of the (A4) ingredient. Therefore, a hardenability constituent containing the (G) ingredient and the (A4) ingredient is before and after storage, and turns into a hardenability constituent with little change of a cure rate. A reactive silicon group of this (G) ingredient and the (A4) ingredient. Since a carbon number of an alkoxy group combined with a silicon atom is 2 to 20, toxic high methenol is not contained in alcohol generated in connection with a hydrolysis reaction of a reactive silicon group when a hardenability constituent carries out condensation hardening, but becomes it with a constituent with high safety.
[0211]
(G) Although it is usable as a many liquid [such as 1 liquid type and a two-component type,] type constituent, when it is considered as 1 liquid type, since said hardenability constituent which consists of an ingredient and a (A4) ingredient has a large effect which makes smell especially change of a cure rate in storage order, it is preferred.
[0212]
(G) An ingredient is a compound which has a reactive silicon group expressed with a general formula (7), and an amino group. As an example of a reactive silicon group expressed with e general formula (7), s triethoxy silyl group, a methyldi ethoxy silyl group, a dimethylethoxy silyl group, an ethyldiethoxy silyl group, a triisopropoxy silyl group, a methyldi isopropoxy silyl group, etc. can be mentioned. An alkoxy group combined with a silicon atom of a reactive silicon group has preferred toxio ethoxy silyl group from a viewpoint or isopropoxy silyl of alcohol generated in connection with a hydrolysis reaction, and its ethoxy silyl group is more preferred. From a viewpoint of a cure rate, as for the number of an alkoxy group combined with one silicon atom of a reactive silicon group, two or more pieces are preferred, and its three pieces are more preferred. The toxicity of alcohol generated in connection with a hydrolysis reaction and a viewpoint of a cure rate to a triethoxy silyl group is the most preferred.
[0213]
As an example of an ingredient, (G) gamma-aminopropyl triethoxysilane, gamma-aminopropyl triisopropoxy silane, gamma-aminopropyl methyldiethoxysilane, gamma-(2-aminoethyl) aminopropyl triethoxysilane, gamma-(2-aminoethyl) aminopropyl triisopropoxy silane, gamma-(2-aminoethyl) aminopropyl methyldiethoxysilane, gamma-ureido propyl triethoxysilane, gamma-ureido propyl triisopropoxy silane, gamma-ureido propylmethyl diethoxysilane, N-phenyl-gamma-aminopropyl triethoxysilane, N-benzyl-gamma-aminopropyl triethoxysilane, N-n-butyl-gamma-aminopropyl triethoxysilane, N-vinylbenzyl gamma-aminopropyl triethoxysilane, N,N'-bis(gamma-triethoxy silyl propyl)ethylenediamine, Amino group content Silang, such as bis(triethoxy silyl propyl)amine and gamma-[2-(2-aminoethyl) aminoathyl] aminopropyl triethoxysilane, can be mentioned: A denatured derivative and s condensation reaction thing of the above-mentioned silane compound can also use the above-mentioned silane compound as a (G) ingredient.
[0214]
The (G) ingredient used for this invention is used in 0.1-10 copies to 100 copies of organic polymers of the (A4) ingredient. It is preferred to use it in 1-5 copies especially. The above-mentioned (G) ingredient may be used only by one kind, and may carry out two or more kind mixing use.
[0215]
(A4) A dehydrator may be added when using as a 1 liquid type constituent a constituent which consists of an ingredient and a (G) ingredient. Especially as said dehydrator, it is not restricted but various kinds of compounds can be used. Since [that a change in physical properties after a silicon compound which has alkoxy silyl groups and does not contain an amino group as a dehydrator storing by care of health at low temperature comparatively since an ester exchange reaction with a reactive silicon group of the (A4) ingredient is late is small and] the drying effect is high, it is desirable. Since a silicon compound which has the Tori alkoxy silyl groups and does not contain an amino group has the higher drying effect, it is prefered, and especially a silicon compound that has a trimethoxysilyl group and does not contain an amino group is preferred. Specifically, alkyltrialkoxysilane, such as vinyltrimetoxysilane, methyl trimetoxysilane, and phenyltrimathoxysilane, is preferred from points, such as the drying effect, hardenability, avsilability, and the tension physical properties of a hardened material.
[0216]
At this invention, it is a general formula as e (H) ingredient (8). :
$-SiR^7_d(OCH_3)_e(OR^8)_{3-d-e}$ (8)
(Among a formula, d R^7 is the organic groups of monovelence of the carbon numbers 1-20 independently, respectively, R^8 of a 3-d-e individual is an organic group of monovelence of the carbon numbers 2-20 independently, and d shows 0, 1, or 2 and, as for e, it shows 1, 2, or 3, respectively.) However, 3-d-e>=0 shall be satisfied. An aminosilane coupling agent which has a basis expressed can be used. General formula (6) which is the (A4) ingredient of this invention about this (H) ingredient :
$-Si(OR^4)_3$ (6)
If it is recuperated beforehend, a hardenability constituent added to an organic polymer which has e basis expressed with (R^4 in a formula is the same as the above). (H) An ester exchange reection between a methoxy silyl group of an ingredient and a reactive silicon group of the (A4) ingredient advances, and e reactant high methoxy silyl group generetes to a reactive silicon group of the (A4) ingredient. A hardenability constituent obtained as a result turns into a hardenability constituent of fast ourability while having outstanding adhesive property, stability, endurance, and creep resistance.
[0217]
(H) Desirable care-of-health conditions of said hardenability constituent which consists of an ingredient and a (A4) ingredient. Since it changes with existence of a transesterification catalyst and its addition, ester exchange reaction activity of a reactive silicon group of the (H) ingredient and the (A4) ingredient, etc., are not generally decided, but as a transesterification catalyst, When it includes an organic tin catalyst or 0.5 copy - about three copies of Ti system catalysts in a system, in a low temperature service, the 10-30 ** thing for which it is recuperated comparatively one week or more is preferred, and it is preferred that more than a day recuperates itself in not less then 30 ** high temperature service.
[0218]
(H) Although it is usable as e many liquid [, such as 1 liquid type and a two-component type,] type constituent, when it is considered as 1 liquid type, since said hardenability constituent which consists of an ingredient and a (A4) ingredient has a remarkable chenge of a cure rate especially by care of health, it is preferred.
[0219]
(H) An ingredient is e compound which has a reactive silicon group expressed with a general formula (8), and an amino group. As an exemple of e reactive silicon group expressed with a general formula

(8), A trimethoxysilyl group, a methyl dimethoxy silyl group, an ethyl dimethoxy silyl group, an ethoxy dimethoxy silyl group, a dimethyl methoxy silyl group, a diethyl methoxy silyl group, a diethoxy methoxy silyl group, etc. can be mentioned. From a viewpoint of ester exchange reaction speed, as for the number of an alkoxy group combined with one silicon atom of a reactive silicon group, two or mors pieces are preferred, and its three pisces are more preferred. Therefors, a trimethoxysilyl group is the most preferred.
[0220]
As an example of an ingredient, (H) gamma-aminopropyl trimethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl ethyl dimethoxysilane, gamma-aminopropyl ethoxy dimethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl ethyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl ethoxy dimethoxysilane, gamma-ureido propyltrimethoxysilane, gamma-ureido propylmethyl dimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, N-benzyl-gamma-aminopropyl trimethoxysilane, N-n-butyl-gamma-aminopropyl trimethoxysilane, N-vinylbenzyl gamma-aminopropyl trimethoxysilane, Amino group content Silang, such as N,N'-bis (gamma-trimethoxysilylpropyl)ethylenediamine, bis(trimethoxysilylpropyl)amine, and gamma-[2-(2-aminoethyl) aminoethyl] aminopropyl trimethoxysilane, can be mentioned. A denatured derivative and a condensation reaction thing of the above-mentioned silane compound can also use the above-mentioned silane compound as a (H) ingredient.
[0221]
The (H) ingredient used for this invention is used in 0.1-10 copies to 100 copies of organic polymers of the (A4) ingradient. It is preferred to use it in 1-5 copies especially. The above-mentioned (H) ingredient may be used only by one kind, and may carry out two or more kind mixing use.
[0222]
In this invention, an epoxy resin can be used as a (I) ingredient. This epoxy resin has a function which raises stability, endurance, and creep resistance further while improving impact strength and tough nature of an organic polymer which are the (A4) ingredients of this invention.
[0223]
As an epoxy resin used as a (I) ingredient of this invention, an epichlorohydrin bisphenol A type epoxy resin, Fire retardancy type epoxy resins, such as epichlorohydrin bisphenol F type epoxy resin and glycidyl ether of tetrabromobisphenol A, Novolak type epoxy resin, a hydrogenation bisphenol A type epoxy resin, A glycidyl ether type epoxy resin of a bisphenol A propylene oxide addition, p-oxybenzoic acid glycidyl ether ester typed epoxy resin, m-aminophenol series epoxy resin, A diaminodiphenylmethane system epoxy resin, a urethane modified epoxy resin, Various cycloaliphatic-epoxy-resin and N,N-diglycidyl aniline, N,N-diglycidyl o-toluidine, Although an epoxidation thing of an unseturation polymer, etc. are illustrated at the time, such as glycidyl ether of polyhydric alcohol, a hydantoin type epoxy resin, and petrolsum resin, at the time, such as triglycidyl isocyanurate, polyalkylene glycol diglycidyl ether, and glycerin, Not a thing limited to these but an epoxy resin currently generally used is used, and it gets. What contains an epoxy group in [two] a molecule at least has high reactivity when hardening, and a hardened material is preferred from points — it is easy to build three-dimensional meshes of a net. As a still more desirable thing, bisphenol A type epoxy resins or novolak type epoxy resin is raised. Ranges of a using rate of these epoxy resin (I) and reactive silicon group containing organic polymer (A4) are (A4)/epoxy resin =100 / 1 - 1/100 in a weight ratio. (A4) If the improvement effect of impact strength of an epoxy resin hardened material, tough nature, stability, endurance, and creep resistance becomes will be hard to be acquired if a rate of a /epoxy resin becomes less than 1/100 and a rate of (A4)/epoxy resin surpasses 100/1, intensity of an organic polymer hardened material will become insufficient. Since a desirable using rate changes with uses of a hardenability constituent, etc., are not generally decided, but. For example, when improving the shock resistance of an epoxy resin hardened material, flexibility, tough nature, peel strength, etc., it is good to carry out 5-100 weight-section use of the (A4) ingredient still more preferably one to 100 weight section to epoxy resin 100 weight section. On the other hand, when improving intensity of a hardened material of the (A4) ingredient, it is good to carry out 5-50 weight-section use of the epoxy resin five to 100 weight section still more preferably especially one to 200 weight section to (A4) ingradient 100 weight section.
[0224]

Naturally a hardening agent which makes a constituent of this invention harden an epoxy resin can be used together. As an epoxy resin hardener which can be used, there is no restriction in particular and an epoxy resin hardener ourrently generally used can be used. Specifically, for example Triethylenetetramine, tetrasthylenapentamine, Diethylamino propylamine, N-aminoethyl piperidina, m-xylylene diamine, m-phenylenediamine, diaminodiphanylmethane, diaminodiphenyl sulfone, The first classes, such as isophoronediamine and amine end polyether, seoond class amines;2,4,6-tris(dimethyl aminomethyl) phenol, The third class amines like tripropylamine, and the salts; polyamide resin; imidazole derivatives; dicyandiamides of these third class amines; Boron trifluoride complex compounds, Phthalic anhydride, hexahydro phthalic anhydride, tetrahydro phthalic anhydride, Anhydrous carboxylic acid; alcohols; phenols; carboxylic acid, such as DODESHINIRU succinyl oxide, pyromellitic dianhydride, and anhydrous KURONEN acid; although compounds, such as a diketone complex compound of aluminum or s zirconium, can be illustrated, it is not limited to these. A hardening agent may also be independent or two or more sorts may be used together.
[0225]
When using a hardening agent of an epoxy resin, the amount used is the range of 0.1 to 300 weight section to epoxy resin 100 weight section.
[0226]
Ketimine can be used as a hardening agent of an epoxy resin. In the state where ketimine does not heve moisture, it exists stably, and it is decomposed into primary amine and ketone by moisture, and produced primary amine serves as a hardening agent of the room-temperature-curing nature of an epoxy resin. If ketimine is used, a 1 liquid type constituent can be obtained. As such ketimine, it can obtain by a condensation reaction of an amine compound and a carbonyl compound.
[0227]
Although what is necessary is just to use a publicly known amine compound and a carbonyl compound for composition of ketimine, As an amine compound, for example, ethylenediamine, propylenediamine, Trimethylene diamine, a tetramethylenediamine, 1,3-diaminobutane, 2,3-diaminobutane, pentamethylene diamine, 2,4-diaminopentane, Diamine;1,2,3-triamino propane, such as hexamethylenediamine, p-phenylene diamine, and p,p'-biphenylene diamine, Multivalent amine, such as triamino benzene, tris(2-aminoethyl) amine, and tetra(aminomethyl) methane; Diethylenetriamine, Polyalkylene polyamine, such as TORIECHIREN triamine and tetraethylenepentamine; Polyoxyalkylene series polyamine;gamma-aminopropyl triethoxysilane, Aminosilanes [, such as N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane and N-(beta-aminoethyl)-gamma-aminopropyl methyl dimethoxysilane,]; etc. are used, and it gets. As a carbonyl compound, acetaldehyde, propionaldehyde, n-butylaldehyde, isobutyraldehyde, diethylacetaldehyde, Aldehyde, such as a glyoxal and benzaldehyde; Cyclopentanone, Cyclic ketone, such as trimethyl cyclopantanone, cyclohexanone, and trimethyl cyclohexanone; Acetone, Methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, Methyl isobutyl ketone, a diethyl ketone, dipropyl ketone, diisopropyl keton, Aliphatic series ketone, such as dibutyl ketone and diisobutyl ketone; beta-dicarbonyl compound [, such as an acetylacetone, methyl acetoacetate, ethyl acetoacetate, dimethyl malonate, diethyl malonate, a malonic acid methylethyl, and dibenzoylmethane,]; etc. oan be used.
[0228]
When an imino group exists in ketimine, an imino group may be made to react to glycidyl ether; glycidyl ester, such as styrene oxide; butyl glycidyl ether and allyl glycidyl ether, etc. Such ketimines may be used independently, two or more kinds may be used together and used for them, 1-100 weight-section use is carried out to epoxy resin 100 weight section, and the amount used changes with kinds of an epoxy resin and ketimine.
[0229]
Various bulking agents other than a minute hollow body of the (F) ingredient may be blended with a hardenability constituent of this invention. It is not limited especially as said bulking agent, but For example, fumes silica, sedimentation nature silica, Reinforcement nature bulking agents, such as a silicic acid anhydride, hydrous silicic acids, and carbon black; Calcium carbonate, Bulking agents, such as magnesium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, and hydrogenation castor oil; fibrous fillers, such as asbestos, glass fiber, and a filament, are illustrated.
[0230]

To obtain a hardenability constituent with high intensity with these bulking agents. Mainly Fumes silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, carbon black, A desirable result will be obtained if a bulking agent chosen from surface treatment detailed calcium carbonate, calcination clay, clay, an active white, etc. is used in the range of 1 - 100 weight section to organic polymer (A) 100 weight section. When elongation wants to obtain a hardenability constituent which is size with low strength, A desirable result will be obtained if a bulking agent mainly chosen from titanium oxide, calcium carbonate, magnesium carbonate, talc, ferric oxide, a zinc oxide, etc. is used in the range of 5 - 200 weight section to organic polymer (A) 100 weight section. Of course, these bulking agents may be used only by one kind, and may mix and use two or more kinds.

[0231]

In a hardenability constituent of this invention, since elongation of a hardened material can be enlarged or a lot of bulking agents can be mixed if a plasticizer is used, using it together with a bulking agent, it is more effective.

[0232]

As this plasticizer, dioctyl phthalate, dibutyl phthalate, Phthalic ester, such as butylbenzyl phthalate; Dioctyl adipate, Aliphatic dibasic acid ester, such as succinic acid isodecyl and dibutyl sebacate; Diethylene glycol dibenzoate, Glycol ester, such as pentaerythritol ester; Butyl oleate, Aliphatic serias ester species, such as methyl acetyl ricinolate; Tricresyl phosphate, Phosphoric ester, such as trioctyl phosphate and phosphoric acid octyldiphenyl; Epoxidized soybean oil, Polyether, such as polyester plasticizer; polypropylene glycols, such as polyestar of epoxy plasticizer; dibasic acid and dihydric alcohol, such as epoxidation linseed oil and epoxy stearic acid benzyl, and a derivative of those; Polly alpha-methylstyrene, Polyatyrene, such as polystyrene; plasticizers, such as polybutadiene, Butadiene Acrylonitrile, polychloroprene, polyisoprene, polybutene, and chlorinated paraffins, can use it independently arbitrarily in a form of two or more kinds of mixtures. A desirable result will be obtained if the amount of plasticizers is used in 100 or less weight sections to organic polymer (A) 100 weight section.

[0233]

A polymeric plasticizer can be used. If a polymeric plasticizer is used, as compared with a case where a low molecule plasticizer which is a plasticizer which does not contain a polymer component in a molecule is used, early physical properties are maintained over a long period of time, and drying property (it is also called paintwork) at the time of applying an alkyd paint to this hardened material can be improved. A vinyl-base polymer produced by polymerizing by various methods in a vinyl system monomer as an example of a polymeric plasticizer; Diethylene glycol dibenzoate, Ester species of polyalkylene glycols, such as triethylene glycol dibenzoate and pentaerythritol ester; Sebacic acid, Dibasic acid and ethylene glycol, such as adipic acid, azelaic acid, and phthalic acid, A diethylene glycol, triethylene glycol, propylene glycol, A polyester plasticizer obtained from dihydric alcohol, such as dipropylene glycol; 500 or more molecular weights, Further 1000 or more polyethylene glycols, a polypropylene glycol, A hydroxyl group of polyether polyol, such as polytetramethylene glycol, or these polyether polyol An ester group, polyether [, such as a derivative changed into an ether group etc.]; — polystyrene [, such as polystyrene and Polly alpha-methylstyrene,], although polybutadiene, polybutene, polyisobutylene, butadiene acrylonitrile, polychloroprene, etc. are mentioned, It is not limited to these.

[0234]

Among these polymeric plasticizers, a polymer of the (A) ingredient and a thing to dissolve are preferred. Polyether and a vinyl-base polymer are preferred. A heat-resistant point to compatibility and weatherability, and a vinyl-base polymer are especially preferred. Also in a vinyl-base polymer, an acrylic polymer and/or an methacrylic system polymer are preferred, and acrylic polymers, such as polyacrylic acid alkyl ester, are still more preferred. Its molecular weight distribution is narrow, since hypoviscosity-izing is possible for a synthetic method of this polymer, it is preferred, and it is still more preferred. [of an atom-transfer-radical-polymerization method] [of a living-radical-polymerization method] It is preferred to use a polymer what is called by a SGO process which obtained an acrylic-acid-alkyl-ester system monomer indicated to JP,2001-207157,A by continuation mass polymerization with an elevated temperature and high voltage.

[0235]

although number average molecular weights of a polymeric plasticizer are 500-15000 preferably, they are 800-10000 more preferably -- further -- desirable -- 1000-8000 -- it is 1000-5000 especially preferably. It is 1000-3000 most preferably. If a molecular weight is too low, a plasticizer can flow out temporally by heat or a rainfall, early physical properties cannot be maintained over a long period of time, and alkyd paintwork cannot be improved. If a molecular weight is too high, viscosity will become high and workability will worsen. Although molecular weight distribution in particular of a polymeric plasticizer is not limited, a narrow thing is preferred and less than 1.80 are preferred. 1.70 or less are more preferred, in addition, 1.60 or less are preferred, 1.50 or less are still more preferred, 1.40 especially or less are preferred, and 1.30 or less are the most preferred.

[0236]

A number average molecular weight of a polymeric plasticizer and molecular weight distribution (Mw/Mn) are measured by the GPC method (polystyrene conversion).

[0237]

Although a polymeric plasticizer does not have a reactive silicon group, it may have a reactive silicon group. When it has a reactive silicon group, it acts as a reaction plasticizer and shift of a plasticizer from a hardened material can be prevented. When it has a reactive silicon group, it averages per molecule and one or less piece and 0.8 more piece or less are preferred. When using a plasticizer which has a reactive silicon group, especially an oxyalkylene polymer which has a reactive silicon group, the number average molecular weight needs to be lower than a polymer of the (A) ingredient.

[0238]

A plasticizer may be used alone and may use two or more sorts together. A low molecule plasticizer and a polymeric plasticizer may be used together. These plasticizers can also be blended at the time of polymer manufacture.

[0239]

The amount of plasticizer used is 20 - 100 weight section still more preferably ten to 120 weight section preferably five to 150 weight section to (A) ingredient 100 weight section. In less than five weight sections, if an effect as a plasticizer stops being revealed and 150 weight sections are exceeded, mechanical strength of a hardened material runs short.

[0240]

It is a general formula in order to improve the activity of a condensation catalyst more in a hardenability constituent of this invention. $R_aSi(OR)_{4-a}$ (R is substitution or an unsubstituted hydrocarbon group of the carbon numbers 1-20 independently among a formula, respectively.) a is 0, 1, 2, or 3. A silicon compound shown may be added. Although limitation is not carried out, as said silicon compound Phenyltrimethoxysilane, Phenylmethyldimethoxysilane, phenyldimathylmethoxysilane, Since the effect that what is an aryl group of the carbon numbers 6-20 accelerates a hardening reaction of a constituent is large, R in general formulas, such as diphenyldimethoxysilane, diphenyl diethoxysilane, and triphenylmethoxysilane, is preferred. Especially diphenyldimethoxysilane and diphenyl diethoxysilane are low cost, and especially since they are easy to receive, they are preferred. As for loadings of this silicon compound, about 0.01-20 weight sections are preferred to (A) ingredient 100 weight section, and its 0.1 - 10 weight section is still more preferred. If loadings of a silicon compound are less than this range, an effect of accelerating a hardening reaction may become small. On the other hand, when loadings of a silicon compound exceed this range, hardness and tensile strength of a hardened material may fall.

[0241]

A physical-properties regulator which adjusts the tractive characteristics of a hardened material generated if needed to a hardenability constituent of this invention may be added. Although not limited especially as a physical-properties regulator, for example Methyl trimetoxysilane, Alkyl alkoxysilane, such as dimethyldimethoxysilane, trimethylmethoxysilane, and n-propyltrimethoxysilane; Dimethyldi iso propenoxysilane, Alkyl iso propenoxysilane, such as methyl TORIISO propenoxysilane and gamma-glycidoxy propylmethyl JIISO propenoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, gamma-glycidoxypropyltrimetoxysilane, Vinyltrimetoxysilane, vinyldimethylmethoxysilane, gamma-aminopropyl trimethoxysilane, The alkoxysilane; silicone varnishes which have functional groups, such as N-(beta-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-mercapto propyltrimethoxysilane, and gamma-mercaptopropylmethyl dimethoxysilane; polysiloxanes are mentioned. By using said physical-properties regulator, hardness when stiffening a

constituent of this invention is raised, or hardness is lowered conversely and elongation after fracture can be taken out. The above-mentioned physical-properties regulator may be used independently, and may be used together two or more sorts.
[0242]
Especially a compound that generates a compound which has e univalent silanol group in intramolecular by hydrolysis has the operation which reduces a modulus of a hardened material without worsening stickiness of the surface of a hardened material. A compound which generates especially a trimethyl silanol is preferred. A compound indicated to JP,H8-117521,A can be raised as a compound which generates a compound which has a univalent silanol group in intramolecular by hydrolysis. A compound which generates a silicon compound which is a derivative of alkyl alcohol, such as a hexanol, octanol, and decanol, and generates R_3SiOH **, such as a trimethyl silanol, by hydrolysis, Trimethylolpropane indicated to JP,H11-241029,A, A compound which generates a silicon compound which is a derivative of polyhydric alcohol whose numbers of hydroxyl groups, such as glycerin, pentaerythritol, or sorbitol, are three or more, and generates R_3SiOH **, such as a trimethyl silanol, by hydrolysis can be raised.
[0243]
A compound which generates a silicon compound which is a derivative of an oxypropylene polymer which is indicated to JP,H7-258534,A, and generates R_3SiOH(s), such as e trimethyl silanol, by hydrolysis can also be raised. A polymer which has a silicon content group which can serve as a monosilanol content compound by e hydrolytic silicon content group and hydrolysis in which bridge construction furthermore indicated to JP,H6-279693,A is possible can also be used.
[0244]
A physical-properties regulator is preferably used in the range of 0.5 - 10 weight section 0.1 to 20 weight section to (A) ingredient 100 weight section.
[0245]
In a hardenability constituent of this invention, a lappet is prevented if needed, and in order to improve workability, a thixotropic grant agent (lappet inhibitor) may be added. Although not limited especially as a lappet inhibitor, metallic soap, such as polyamide wax; hydrogenation castor oil derivative; calcium stearate, aluminum stearate, and barium stearate, is mentioned, for example. These thixotropic grant agents (lappet inhibitor) may be used independently, and may be used together two or more sorts. A thixotropic grant agent is used in the range of 0.1 - 20 weight section to (A) ingredient 100 weight section.
[0246]
A compound which contains an epoxy group in one molecula in a constituent of this invention can be used. If e compound which has an epoxy group is used, the stability of a hardened material can be improved. Compounds shown in epoxidation unsaturation oil and fat, epoxidation unsaturation fatty acid ester, alicycle fellows epoxy compounds, and an epichlorohydrin derivative as a compound which has an epoxy group, these mixtures, etc. can be illustrated. Specifically, epoxidized soybean oil, epoxidation linseed oil, a di(2-ethylhexyl) 4,5-epoxy cyclohexane-1,2-JIKABOKISHI rate (E-PS), epoxy octyl stearate, epoxy butyl stearate, etc. are raised. Especially in these, E-PS is preferred. An epoxy compound is good to use it in the range of 0.5 - 50 weight section to (A) ingredient 100 weight section.
[0247]
An oxygen hardenability substance can be used for a constituent of this invention. To an oxygen hardenability substance, an unsaturated compound which can react to oxygen in the air can be illustrated, it reacts to oxygen in the air, a cured film is formed near the surface of a hardened material, and an operation of preventing adhesion of stickiness of the surface, garbage on the surface of a hardened material, and dust is carried out. Drying oil represented with tung oil, linseed oil, etc. by exemple of an oxygen hardenability substance, Various alkyd resins produced by denaturalizing this compound; An acrylic polymer which denaturalized with drying oil. Epoxy system resin, silicon resin; Butadiene, chloroprene, isoprene, Diene series, such as 1,3-pentadiene, a polymerization or 1,2-polybutadiene produced by making carry out copolymerization, Liquefied polymers, such as a polymer of 1,4-polybutadiene, C5 - C8 diene, NBR produced by making carry out copolymerization of these diene series and the monomers which have copolymeric, such as acrylonitrile and styrene, so that

diene series may serve as a subject, Liquefied copolymers, those various denaturetion things, etc. (e mallein-ized denaturation thing, a boiled oil denaturation thing, etc.), such as SBR, are mentioned. These may be used independently and may be used together two or more sorts. Especially among these, tung oil and a liquefied diene system polymer are preferred. Concomitant use of a catalyst and a metal drier which promote an oxidation hardening reaction may heighten an affect. As these catalysts and metal driers, metal salt, such as cobalt naphthanate, lead naphthenate, a naphthenic acid zirconium, octylic acid cobalt, and an octylic acid zirconium, an amine compound, etc. are illustrated. It is a best still more preferred to use it in the range of 0.1 - 20 weight section to (A) ingredient 100 weight section, and the amount of oxygen hardenability substance used is 0.5 - 10 weight section. If an improvement of stain resistance becomes less enough when said amount used will be less than 0.1 weight sections, and 20 weight sections are surpassed, a tendency for the tractive characteristics of a hardened material, etc. to be spoiled will arise. An oxygen hardenability substance is good to use it, using together with e photoresist substance as indicated to JP,H3-160053,A.
[0248]
A photoresist substance can be used for a constituent of this invention. If a photoresist substance is used, a coat of a photoresist substance is formed in the hardened material surface, and stickiness of a hardened material and the weatherability of a hardened material can be improved. By operation of light, molecular structure causes a chemical change considerably for a short time, and a photoresist substance produces physical-properties change of hardening etc. Many things, such as a constituent containing an organic monomer, oligomer, resin, or them, are known by this kind of compound, and commercial arbitrary things can be adopted as it. As a typical thing, an unsaturation acrylic compound, polycinnamic acid vinyl, or azide-ized resin can be used. As an unsaturation acrylic compound, acrylic or an methacrylic system unsaturation group 1 thru/or a monomer which it has partly, it is mixtures, such as oligomer or it, and monomers, such as propylene (or butylene, ethylene) GURIKORUJI (meta) acrylate and neopentyl GURIKORUJI (meta) dimethacrylate, or with a molecular weight of 10,000 or less oligoesters is illustrated. Specifically, For example, special acrylate. ARONIKKUSU M-210 (2 Functional), ARONIKKUSU M-215, ARONIKKUSU M-220, ARONIKKUSU M-233, ARONIKKUSU M-240, ARONIKKUSU M-305 or ARONIKKUSU M-309, ARONIKKUSU M-245; (three organic functions), ARONIKKUSU M-306, ARONIKKUSU M-310, Although ARONIKKUSU M-315, ARONIKKUSU M-320, ARONIKKUSU M-325, (polyfunctional) ARONIKKUSU M-400, etc. can be illustrated, a compound containing especially an acrylic functional group is preferred, and e compound which averages in one molecule and contains the three or more functional groups is preferred. (Each ARONIKKUSU is a product of Toagosei chemical industry Incorporated company above.)
A polycinnamic acid vinyl derivative of many besides what is a photopolymer which uses a cinnamoyl group as a sensitization group as polycinnamic acid vinyl, and esterified polyvinyl alcohol with cinnamic acid is illustrated. A azide-ized resin is known as a photopolymer which uses an azido group as a sensitization group, usually, a "photopolymer" (Showa 47(1972) -- on March 17) besides [which added a diazido compound es e sensitizing agent] a rubber sensitizing solution [and] printing society publication part issue, and the 93rd page - 106th page - 117th page - have detailed illustration -- these -- a sensitizer can be used, being able to mix and adding [it can be independent, or] if needed. Addition of accelerators, such as sensitizers, such as ketone and e nitro compound, and amines, may heighten an effect. A photoresist substance is good to use it in the range of 0.5 - 10 weight section preferably 0.1 to 20 weight section to (A) ingredient 100 weight section, and in 0.1 or less weight section, since there is no effect which improves weatherability. and a hardened material becomes hard too much and produces a cracking crack in 20 or more weight sections, it is not desirable.
[0249]
An antioxidant (antiaging agent) can be used for a constituent of this invention. If an antioxidant is used, the weatherability of a hardened material can be improved. Although a hindered phenol system, a mono- phenol system, a bisphenol system, and a polyphenol system can be illustrated as an antioxidant, especially a hindered phenol system is preferred. Similarly, Tinuvin 622LD, tinuvin 144;CHIMASSORB944LD, CHIMASSORB119floor-line(all are Ciba-Geigy Japan, Inc. make above);MARK LA-57, MARK LA-62, MARK LA-67, and MARK. LA-63 and MARK. LA-68. (All are ADEKAAGASU chemicals incorporated company make above);. A hindered amine light stabiliser

shown in SANORU LS-770, SANORU LS-765, SANORU LS-292, SANORU LS-2626, SANORU LS-1114, and SANORU LS-744 (all are the Sankyo Co., Ltd. make above) can also be used. An example of an antioxidant is indicated also to JP,H4-283259,A or JP,H9-194731,A. It is at best still more preferred to use it in the range of 0.1 - 10 weight section to (A) ingredient 100 weight section, and the amount of antioxident used is 0.2 - 5 weight section.
[0250]
Light stabilizer can be used for a constituent of this invention. If light stabilizer is used, photooxidation degradation of a hardened material can be prevented. Although a benzotriazol system, a hindered amine system, a benzoate system compound, etc. can be illustrated as light stabilizer, especially a hindered amine system is preferred. It is at best still more preferred to use it in the range of 0.1 - 10 weight section to (A) ingredient 100 weight section, and the amount of light stabilizer used is 0.2 - 5 weight section. An example of light stabilizer is indicated also to JP,H9-194731,A.
[0251]
When an unsaturation acrylic compound is used especially as a photoresist substance in a constituent of this invention, it is preferred to use a tertiary amine content hindered amine light stabilizer as a hindered amine light stabilizer as indicated to JP,H5-70531,A because of preservation stability improvement of a constituent. As a tertiary amine content hindered amine light stabiliser, ** tinuvin 622LD and tinuvin 144; CHIMASSORB119floor line. (All are the Ciba-Geigy Japan, Inc. make above);MARKLA-57, LA-62, LA-67, LA-63 (all are ADEKAAGASU chemicals incorporated company make above); SANORU LS-765, LS-292, LS-2626, LS-1114, LS-744. (All are the Sankyo Co., Ltd. make above) etc. — light stabilizer can be illustrated.
[0252]
An ultraviolet ray absorbent can be used for a constituent of this invention. If an ultraviolet ray absorbent is used, the surface weatherability of a hardened material can be improved. Although a benzophenone series, a benzotriazol system, a salicylate series, a substitution tolyl system, a metal chelate system compound, etc. can be illustrated as an ultraviolet ray absorbent, especially a benzotriazol system is preferred. It is at best still more preferred to use it in the range of 0.1 - 10 weight section to (A) ingredient 100 weight section, and the amount of ultraviolet ray absorbent used is 0.2 - 5 weight section. It is preferred to use together and use a phenol system, a hindered phenolic antioxidant, a hindered amine light stabiliser, and a benzotriazol system ultraviolet ray absorbent.
[0253]
An ingredient which limitation in particular does not have in the method of preparation of a hardenability constituent of this invention, for example, was described above is blended, it kneads under ordinary temperature or heating using a mixer, a roll, a kneader, etc., or an ingredient is dissolved using a little suitable solvents, a usual method of mixing is adopted, and it gets. A many liquid [, such as 1 liquid type and a two-component type,] type compound can also be made and used by combining these ingredients suitably.
[0254]
If a hardenability constituent of this invention is exposed into the atmosphere, by operation of moisture, it will form network structure in three dimensions, and will harden it promptly to a solid which has rubber-like elasticity.
[0255]
It faces using a hardenability constituent of this invention. If needed Adhesive improving agents other than an aminosilane, a physical-properties regulator, It is possible to add suitably various additive agents, such as a preservation stability improving agent, an ultraviolet ray absorbent, a metal deactivator, anti-ozonant, light stabilizer, amine system radical chain inhibitor, the Lynn system peroxide decomposition agent, lubricant, paints, and a foaming agent.
[0256]
A hardenability constituent of this invention can be used for sealant, such as a binder, a building, a marine vessel, and a super highway, adhesives, modeling material, a vibroisolating material, a sound deadener, a sound insulating material, a charge of foam, a paint, a gunning material, etc. Electrical insulation materials, such as electric electronic component materials, such as a solar cell rear-face sealing agent, pre-insulation an electric wire, material for cables, Elastic adhesives, powder coatings, casting material, a medical-application rubber material, a medical-application binder, A sealing material for masonry joints of sheathing materials, such as a medical equipment sealant, food packing

material, and a sizing board. A coating material, a primer, a conductive material for electromagnetic wave cover, a thermally conductive material, A charge of a hot melt material, a potting agent for electric electrons, a film, a gasket, It is available for various uses, such as a fluid-sealant agent used in various molding materials and wired sheet glass and a sealing agent for rust prevention / water proof of the glass laminate end face (cut section), autoparts, electrical machinery parts, several kinds of machine part, etc. Since, or help of a primer is borrowed and it may stick to substrates of a **** large area, such as glass, porcelain, wood, metal, and a resin-molding thing, it is usable also as various seal constituents and adhesion constituents of a type. A hardenability constituent of this invention from excelling in stability, endurance, and creeping property. Adhesives for interior panels, adhesives for face panels, adhesives for tiling, adhesives for stone tensions, Ceiling finishing adhesives, floor finishing adhesives, adhesives for finishing of wall, adhesives for car panels. It is desirable, especially when it is considered as the electrical and electric equipment, an electron and adhesives for precision-mechanical-equipment assemblies, a sealing material for direct grazing, a sealing material for multiple glass, a sealing material for speed signal generator construction methods, or a sealing material for working joint of a building and uses.
[Effect of the Invention]
[0257]
The hardenability constituent of this invention is excellent in stability, endurance, and creep resistance.
[Best Mode of Carrying Out the Invention]
[0258]
Although working example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these working example.
[0259]
(Synthetic example 1)
Use polyoxypropylene triol of the molecular weight 3,000 [about] as an initiator, and propylene oxide is polymerized in a zinc hexa cyanocobaltate glyme complex compound catalyst. Number average molecular weight about 26,000 (polystyrene reduced molecular weight in which the column measured the solvent using THF using the TOSOH TSK-GEL H type using TOSOH HLC-8120GPC as a liquid-sending system) polypropylene oxide was obtained. Then, the methanol solution of NaOMe of the equivalent was added 1.2 times to the hydroxyl group of this hydroxyl group and polypropylene oxide, and methanol was distilled off, and also the allyl chloride was added, and the hydroxyl group of the end was changed into the allyl group. Decompression devolatilization removed the unreacted allyl chloride. To allyl end polypropylene oxide 100 weight section which is not refined [which was obtained], n-hexane 300 weight section, After it carried out mixed stirring of the water 300 weight section further at the hexane solution obtained by centrifugal separation removing water after carrying out mixed stirring of the water 300 weight section and centrifugal separation removed water again, decompression devolatilization removed hexane. By the above, the end obtained 3 organic-functions polypropylene oxide of the number average molecular weight 26,000 [about] which is an allyl group.
[0260]
150 ppm of platinum content 3wt% of platinum vinyl siloxane complexes isopropanol solutions are made into a catalyst to allyl end polypropylene oxide 100 obtained weight section. It was made to react to methyl dimethoxysilane 1.4 weight section at 90 ** for 5 hours, and the methyl dimethoxy silyl group end polyoxyalkylene series polymer (A-1) was obtained. Measurement by ^{1}H-NMR (it measures in a $CDCl_3$ solvent using JEOL JNM-LA400) averaged the methyl dimethoxy silyl group of the end per molecule, and they were 2.3 pieces.
[0261]
(Working example 1-4 and comparative examples 1-2)
Organic polymer (A-1) 100 weight section which has the reactive silicon group obtained in the synthstic example 1 according to the combination formula shown in Table 1, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo maks.) SANORU LS7701 weight section and an ultraviolet ray

absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilana (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimathoxysilane (the Nippon Unioar make.) A-1120) silicate (made in a col coat.) given in three weight sections and Table 1 Mada in an ethyl ailicata 28; col coat, ethyl silicate 40; Made in a col coat, a curing catalyst (tha Japanesa east — transformation — make and the dibutyltin bisacetylacetonate (trade name: U-220); Japanese east — transformation — make and the product made from neo decanoic acid tin (divalent) (trade name: U-50); Japan epoxy resin.) given in the amount part of methylsilicate 51 duplexs, and Table 1 Neo decanoic acid (trade name: BASA tick 10); the description to Table 1 of the Wako Pure Chemical Industries make and lauryl amine carried out number-of-copies addition, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.

[0262]

(Hauling physical properties of a hardened material)

It was 23 **x3 +50 **x recuperated in the class product of Table 1 on the 4th, and the sheet about 3 mm thick was created. [per day] It examined by having pierced this sheet to the No. 3 dumbbell type, and having pulled by a part for 200-mm/in hauling speed, and was extended at the time of intensity (MPa) and Eb:fractura at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A reault is shown in Table 1.

[0263]

(Recovery)

It was 23 **x3 +50 **x recuperated in the olass product of Table 1 on the 4th, and tha sheet about 3 mm thick was created. [per day] This sheet was pierced to the No. 3 dumbbell type, and where 20 mm is pulled to 40 mm between the marked lines (100% extension), it fixed at 60 ** for 24 hours. The recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. It means that the one where the recovery is larger is excellent in stability. A result is shown in Table 1.

[0264]

(Creep measurement using the piece of a dumbbell)

It was 23 **x3 +50 **x recuperated in the class product of Table 1 on the 4th, and the sheet about 3 mm thick was created. [per day] This sheet was pierced to the No. 3 dumbbell type, and the marked line of 20 mm of intervals was described. The end of this piece of a dumbbell was fixed in 60 ** oven, and the piece of a dumbbell was hung. 0.4 time as much load as M50 value obtained by the above-mentioned tension physical-properties measurement of this hardened material was imposed on the lowar end of the hung piece of a dumbbell. The displacement differance of tha distance between the marked lines of 200 hours after immediataly after impoaing load was measured. It means that the one where a displacemant differenca is smallar is excellent in creep resistance. A rasult ia shown in Table 1.

[0265]

[Table 1]

組成（重量部）			実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2
有機重合体	（A）成分	A－1	100	100	100	100	100	100
充填材		白艶華CCR	120	120	120	120	120	120
		タイペークR-820	20	20	20	20	20	20
可塑剤		DIDP	55	55	55	55	55	55
チクソ性付与剤		ディスパロン #6500	2	2	2	2	2	2
光安定剤		サノールLS-770	1	1	1	1	1	1
紫外線吸収剤		チヌビン327	1	1	1	1	1	1
酸化防止剤		ノクラックSP	1	1	1	1	1	1
脱水剤		A-171	2	2	2	2	2	2
接着性付与剤		A-1120	3	3	3	3	3	3
シリケート	（B）成分	エチルシリケート28	2	2				
		エチルシリケート40			2			
		メチルシリケート51				2		
硬化触媒	有機スズ	ネオスタンU-220	2				2	
	カルボン酸スズ塩	ネオスタンU-50		3.4	3.4	3.4		3.4
	カルボン酸	バーサティック10		1.2	1.2	1.2		1.2
	アミン	ラウリルアミン		0.75	0.75	0.75		0.75
復元率		(%)	54	84	88	86	26	80
クリープ		(mm)	15.1	1.6	1.2	1.4	30.2	2.2
硬化物物性	M50	(MPa)	0.53	0.46	0.48	0.50	0.42	0.43
	Tb	(MPa)	2.00	2.27	2.61	2.35	1.96	2.23
	Eb	(%)	297	400	442	389	385	480

[0266]

As shown in the comparative example 1 of Table 1, when organic tin (U-220) is used as a curing catalyst, especially the recovery of creep resistance is low bad silicate additive-free. However, as shown in working example 1, stability and creep resistance are notably improved by addition of silicate. As shown in the comparative example 2, when organic tin (U-220) is used for ****, carboxylic acid tin salt (neo SUTAN U-50), etc. as a curing catalyst, stability and creep resistance also with good silicate additive-free are shown, but. As shown in working example 2-4, stability and craap resistance further outstanding by silicate addition were shown. The ethyl silicata 40 and tha methylsilicate 51 which were usad in working example 3-4 are a condensate of a tetraethoxysilane and a tetramethoxy silane, respectively, and showed the eapacially outstanding effect.

[0267]

(Synthetic example 2)
Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 14,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Allyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1. To this allyl end polypropylene oxide, in the same procedure as the synthetic example 1, it was made to react to trimethoxysilane and the polyoxyalkylene series polymer (A-2) which has an average of 1.5 trimethoxysilyl groups at the end was obtained.
[0268]
(Synthetic example 3)
To the allyl end polypropylene oxide obtained in the synthetic example 2, in the same procedure as the synthetic example 1, it was made to react to triethoxysilane and the polyoxyalkylene series polymer (A-3) which has an average of 1.5 triethoxy silyl groups at the end was obtained.
[0269]
(Synthetic example 4)
To the allyl end polypropylene oxide obtained in the synthetic example 2, in the same procedure as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-4) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.
[0270]
(Working example 5-11 and comparative examples 3-5)
Organic polymer (A-2-4) 100 weight section which has the reactive silicon group obtained in the synthetic examples 2-4 according to the combination formula shown in Table 2, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section. Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP12 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make.) SANORU LS7701 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section. The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) Three weight sections, number of copies given [silicate (made in a col coat, methylsilicate 51)] in Table 2, the curing catalyst (Japanese east transformation make and dibutyltin bisacetylacetonate (trade name: U-220); the Sankyo Organic Chemicals make, a dibutyltin JIRAURI rate (trade name: STANN BL)) of the (D) ingredient given in Table 2, or the curing catalyst (the Japanese east -- transformation -- make.) of the (C) ingradiant The description to Table 2 of neo decanoic acid tin (divalent) (trade name: U-50) and amine (the Wako Pure Chemical Industries make, lauryl amine) carried out number-of-copies addition, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.
[0271]
It examined by having pulled by the same method as the above-mentioned using the class product of Table 2, and was extended at the time of intensity (MPa) and Eb:fracture at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A result is shown in Table 2.
[0272]
The recovery was measured by the same method as the above-mentioned using the class product of Table 2. However, the stretched state was fixed at 23 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. A result is shown in Table 2.
[0273]
(Creep measurement using a shear sample)
The displacement difference with the 140-hour back immediately after creating the ** sample which is not carried an area of 20 mm x 25 mm and 1 mm in thickness using the class product of Table 2, imposing 0.1MPa load for what recuperated [23 **x3 +50 **x] itself on the 4th in 60 ** oven, and imposing load was measured. [per day] The displacement difference made O x for the thing below

0.4 mm, and the displacement difference carried out a thing of 0.4 mm or more. A result is shown in Table 2.
[0274]
[Table 2]

組成（重量部）		反応性ケイ素基の構造	実施例 5	6	7	8	9	10	11	比較例 3	4	5
有機重合体 （A1）成分	A－2	トリメトキシシリル基	100	100								
	A－3	トリエトキシシリル基			100	100	100	100	100			
	A－4	メチルジメトキシシリル基								100	100	100
充填材		白艶華CCR	120	120	120	120	120	120	120	120	120	120
		タイペークR-820	20	20	20	20	20	20	20	20	20	20
可塑剤		DIDP	12	12	12	12	12	12	12	12	12	12
チクソ性付与剤		ディスパロン #6500	2	2	2	2	2	2	2	2	2	2
光安定剤		サノールLS-770	1	1	1	1	1	1	1	1	1	1
紫外線吸収剤		チヌビン327	1	1	1	1	1	1	1	1	1	1
酸化防止剤		ノクラックSP	1	1	1	1	1	1	1	1	1	1
脱水剤		A-171	2	2	2	2	2	2	2	2	2	2
接着性付与剤		A-1120	3	3	3	3	3	3	3	3	3	3
シリケート （B）成分		メチルシリケート51						2				
硬化触媒 （D）成分		ネオスタンU-220	0.2		0.2	2		2		0.2	2	
		Stann BL		0.3			3					3
（C）成分		ネオスタンU-50							3.4			
アミン		ラウリルアミン							0.75			
復元率		(%)	93	93	93	93	94	96	96	67	47	64
クリープ（せん断）			○	○	○	○	○	○	○	×	×	×
硬化物物性 M50		(MPa)	0.94	0.95	1.13	0.92	0.92	1.15	0.94	1.01	0.85	0.82
Tb		(MPa)	2.24	2.20	2.61	2.35	2.08	2.20	2.18	2.83	2.84	2.70
Eb		(%)	193	196	184	208	208	167	216	269	340	370

[0275]
When the reactive silicon group of an end uses the organic polymer (A-2-3) which is the Tori alkoxy silyl groups from comparison with working example 5-9 of Table 2, and the comparative examples 3-5, stability and creep resistance are improved notably. Working example 10 which added silicate, and working example 11 using carboxylic acid tin salt (neo SUTAN U-50) as a curing catalyst showed the further outstanding recovery.
[0276]
(Synthetic example 5)
To the allyl end polypropylene oxide obtained in the synthetic example 1, in the same procedure as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-5) which has an average of two methyl dimethoxy silyl groups at the end was obtained.
[0277]
(Synthetic example 6)
Use polyoxypropylene triol of the molecular weight 3,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 26,000 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Metallyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1 except making an allyl chloride into chloridation metallyl. 0.5 copy of platinum content 3wt% of platinum vinyl siloxane complexes isopropanol solution is made into a catalyst to this metallyl end polypropylene oxide 100 weight section, oxygen — 6vol% — mixed sulfur at a rate of 1 eq/Ptleq under the atmosphere of the nitrogen to contain, it was made to react to methyl dimethoxysilane 3.2 weight section at 90 ** for 5 hours, and the polyoxyalkylene series polymer (A-6) which has an average of 2.8 methyl dimethoxy silyl groups at the end was obtained.
[0278]
(Working example 12-14 and comparative example 6)
Organic polymer (A-1, A-4-6) 100 weight section which has the reactive silicon group obtained in the synthetic example 1 and the synthetic examples 4-6 according to the combination formula shown in Table 3, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP35 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make.) SANORU LS7701 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, As the amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (Nippon Unicar make, A-1120) 3 weight section, and a curing catalyst, Carboxylic acid tin salt (Japanese east transformation make, neo decanoic acid tin (divalent) (trade name: U-50)) 3.4 weight section, Carboxylic acid (product made from Japan epoxy resin, neo decanoic acid (trade name: BASA tick 10)) 1.2 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section are added. After kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.
[0279]
It examined by having pulled by the same method as the above-mentioned using the class product of Table 3, and was extended at the time of intensity (MPa) and Ebfracture at the time of M50:50% hauling modulus (MPa) and Tbfracture, and (%) was measured. A result is shown in Table 3.
[0280]
The recovery was measured by the same method as the above-mentioned using the class product of Table 3. However, the stretched state was fixed at 60 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. A result is shown in Table 3.
[0281]
The displacement difference of the distance between the marked lines of 200 hours after immediately

after performing creep measurement using the piece of a dumbbell, and imposing load by the same method as the method of working example 1-4, using the class product of Table 3, was measured. A result is shown in Table 3.
[0282]
[Table 3]

組成（重量部）		1分子あたりの反応性ケイ素基	実施例 12	13	14	比較例 6
有機重合体（A2）成分	A-5	2.0個	100			
	A-1	2.3個		100		
	A-6	2.8個			100	
	A-4	1.5個				100
充填材	白艶華CCR		120	120	120	120
	タイペークR-820		20	20	20	20
可塑剤	DIDP		55	55	55	55
チクソ性付与剤	ディスパロン#6500		2	2	2	2
光安定剤	サノールLS-770		1	1	1	1
紫外線吸収剤	チヌビン327		1	1	1	1
酸化防止剤	ノクラック200		1	1	1	1
脱水剤	A-171		2	2	2	2
接着性付与剤	A-1120		3	3	3	3
硬化触媒	新オクチル酸スズ塩		3.4	3.4	3.4	3.4
	脂肪族アミン		1.2	1.2	1.2	1.2
	ラウリルアミン		0.75	0.75	0.75	0.75
復元率		(%)	78	81	86	73
クリープ		(mm)	2.5	2.2	1.3	3.2
硬化物物性	M50	(MPa)	0.35	0.43	0.68	0.38
	Tb	(MPa)	2.39	2.30	1.87	2.02
	Eb	(%)	601	483	273	502

[0283]
Comparison with working example 12-14 of Table 3 and the comparative example 6 shows that the organic polymer with many reactive silicon groups per molecule (A-1, A-5-6) is excellent in stability and creep resistance.
[0284]
(Synthetic example 7)
Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl

group end polypropylene oxide of tha number average molecular weight 28,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Metallyl end polypropylene oxide was obtained in the same procedure as the synthetic example 6. To this metallyl end polypropylene oxide, in tha same procedure as the synthetic example 6, it was made to react to methyl dimethoxysilane and the polyoxyalkylena series polymar (A-7) which has an average of 1.9 methyl dimathoxy silyl groups at the and waa obtained.

[0285]

(Synthetic example 8)

To the metallyl end polypropylene oxide obtained in the synthetic example 7, in the same procedure as the synthetic example 6, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-8) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.

[0286]

(Synthetic example 9)

Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 28,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyma complex compound catalyst is used, Allyl end polypropylene oxide was obtained in tha aama procedure as the synthetic example 1. To this allyl end polypropylene oxide, in the same procedure as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene seriaa polymar (A-9) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.

[0287]

(Working example 15-16 and comparativa examplas 7-8)

Organic polymer (A-4, A-7-9) 100 weight section which has the reactive silicon group obtained in the synthetic example 4 and the synthetic examples 7-9 according to the combination formula shown in Table 4, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make.) SANORU LS770l weight section and an ultraviolet ray absorbent (made in Tiba Speciality Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) Three weight sections and the amount part of curing catalyst dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs were added, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.

[0288]

It examined by having pulled by the same method as the above-mentioned using the class product of Table 4, and was extended at the time of intensity (MPa) and Eb:fracture at the time of M50:50% hauling modulus (MPa) and Tb:fracture, and (%) was measured. A result is shown in Table 4.

[0289]

The recovery was measured by the same method as the above-mentioned using the class product of Table 4. However, the stretched state was fixed at 23 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 24 hours afterward. A result is shown in Table 4.

[0290]

The displacement difference of the distance between the marked lines of 45 hours after immediately after performing creep measurement using the piece of a dumbbell, and imposing load by the same method as the method of working example 1-4, using the class product of Table 4, was measured. A result is shown in Table 4.

[0291]

[Table 4]

組成（重量部）			反応性ケイ素基導入 前の末端基の構造	1分子あたりの 反応性ケイ素基	実施例		比較例	
					15	16	7	8
有機重合体	（A3）成分	A－7	メタリル基	1.9個	100			
		A－8	メタリル基	1.5個		100		
		A－9	アリル基	1.5個			100	
		A－4	アリル基	1.5個				100
充填材			白艶華CCR		120	120	120	120
			タイペークR-820		20	20	20	20
可塑剤			DIDP		55	55	55	55
チクソ性付与剤			ディスパロン#6500		2	2	2	2
光安定剤			サノールLS-770		1	1	1	1
紫外線吸収剤			チヌビン327		1	1	1	1
酸化防止剤			ノクラックSP		1	1	1	1
脱水剤			A-171		2	2	2	2
接着性付与剤			A-1120		3	3	3	3
硬化触媒			オクチル酸Sn-220		2	2	2	2
硬化速			(%)		86	84	74	75
クリープ			(mm)		15	22	44	41
硬化物物性	M50		(MPa)		0.41	0.21	0.19	0.39
	Tb		(MPa)		2.71	3.02	2.60	1.90
	Eb		(%)		852	1019	1018	403

[0292]

Comparison with working example 15-16 of Table 4 and tha comparative examples 7-8 shows that the organic polymer (A-7-8) which introduced the reactive silicon group to the metallyl group end

organicity polymer is excellent in stability and creep resistance.
[0293]
(Synthetic example 10)
To the allyl end polypropylene oxide obtained in the synthetic example 1, in the same procedure as the synthetic example 1, it was made to react to triethoxysilane and the polyoxyalkylene series polymar (A-10) which has an average of 2.3 triethoxy silyl groups at the end was obtained.
[0294]
(Working example 17 and comparative examples 9-10)
Organic polymer (A-1, A-10) 100 weight section which has the reactive silicon group obtained in the synthetic example 1 and the synthetic example 10 according to the combination formula shown in Table 5, Surface treatment colloid calcium carbonate (product made from Solvay, Winnofil SPM) 120 weight section, Titanium oxide (product made from Kerr-McGee, RFK-2) 20 weight section, DIUP50 weight section, Thixotropic grant agent (product made from Cray Valley, Crayvallasuper) 5 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, As a dehydrator, the amount part of vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, gamma-aminopropyl triethoxysilane (the Nippon Unicar make,) which is the (G) ingredient as an adhesion grant agent A-1100) Or add N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (Nippon Unicar make, A-1120) 3 weight section and the amount part of curing catalyst dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs. After kneading in the stata where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained.
[0295]
The recovery was measured by the same method as the above-mentioned using the class product of Table 5. However, the stretched state was fixed at 60 ** 100% for 24 hours this time, and the recovery was measured from the rate which opened this wide at 23 ** and the marked line restored 1 hour afterward. A result is shown in Table 5.
[0296]
The displacement difference of the distance between the marked lines of 140 hours after immediately after performing creep measurement using a shear sample and imposing load by the same method as the method of working example 5-11, using the class product of Table 5, was measured. As for the valuation basis, the displacement difference made 0 x for the thing below 0.4 mm, and the displacement difference carried out a thing of 0.4 mm or more. A result is shown in Table 5.
[0297]
(Hardenability of a hardenability constituent)
The class product of Table 5 was thinly lengthened in thickness of about 3 mm, and time (leather-covered time) until the surface stretches a hide under 23 ** and 50% of humidity RH conditions was measured. The one where leather-covered time is shorter means that hardenability is excellent. A result is shown in Table 5.
[0298]
[Table 5]

組成（重量部）		反応性ケイ素基の構造		実施例 17	比較例 9	比較例 10
有機重合体	（A4）成分	A－10	トリエトキシシリル基	100	100	
		A－1	メチルジメトキシシリル基			100
充填材		Winnofil SPM		120	120	120
		RFK-2		20	20	20
可塑剤		DIUP		50	50	50
チクソ性付与剤		Crayvallac super		5	5	5
光安定剤		サノールLS-770		1	1	1
紫外線吸収剤		チヌビン327		1	1	1
酸化防止剤		ノクラックSP		1	1	1
脱水剤		A-171		2	2	2
接着性付与剤	（G）成分	A-1100	トリエトキシシリル基	3		
		A-1120	トリメトキシシリル基		3	3
硬化触媒		ネオスタンU-220		2	2	2
復元率		(%)		87	85	25
クリープ（せん断）				○	○	×
皮張時間	貯蔵前	(min)		20	15	15
	貯蔵後	(min)		20	5	15

[0299]
If the aminosilane which has a triethoxy silyl group which is the (G) ingredient as an adhesive grant agent is combined with the end of the (A4) ingredient using the polymar which has a triethoxy silyl group as an organic polymer as shown in working example 17 of Table 5, Excelling in stability and creep resistance, change of the skinning time in storage order is small, and storage stability is good.

[0300]
(Working example 18 and comparative examples 11-12)
Organic polymer (A-2) 100 weight section which has the reactive silicon group obtained in the synthetic example 2 according to the combination formula shown in Table 6, as DIDP30 weight section and a dehydrator -- triethoxysilane (made in a col coat.) the N-beta-(aminoathyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) which is the (H) ingredient as the amount part of ethyl silicate 28 duplexs, and an adhesion grant agent A-1120) or N-beta-(aminoethyl)-gamma-aminopropyl triethoxysilane (the Shin-Etsu Chemical make.) It added, KBE-6033 weight section and the amount part of curing catalyst dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs were sealed in the glassware which carried out the nitrogen purge, and 1 liquid mold-curing nature constituent was obtained. In the comparative example 11, the leather-covered time test was performed under 50% of 23 ** humidity RH conditions, without recuperating oneself in this 1 liquid mold-curing nature constituent. In working example 18 and the comparative example 12, after promoting the ester exchange reaction between reactive silicon groups by recuperating oneself for seven days at 50 ** in these 1 liquid mold-curing nature constituents, the leather-covered time test was performed under 50% of 23 ** humidity RH conditions. A result is shown in Table 6.
[0301]
[Table 6]

組成（重量部）		反応性ケイ素基の構造	実施例 18	比較例 11	比較例 12
有機重合体	（A4）成分	A－2 トリエトキシル基	100	100	100
可塑剤		DIDP	30	30	30
脱水剤		エチルシリケート28	2	2	2
接着性付与剤	（H）成分	A-1120 トリメトキシル基	3	3	
		KBE-603 トリエトキシル基			3
硬化触媒		ネオスタンU-220	2	2	2
50℃×7日の養生			有	無	有
皮張時間		(min)	3	13	12

[0302]
As shown in working example 18 of Table 6, the polymer which has a triethoxy silyl group is used for the end of the (A4) ingredient as an organic polymer. If the aminosilane which has a methoxy silyl

group which is the (H) ingredient as an adhesive grant agent is combined and an ester exchange reaction is promoted by care of health. the hardenability of an organic polymer can be raised notably.
[0303]
(Working example 19-20 and comparative example 13)
Organic polymer (A-10) 100 weight section which has the reactive silicon group obtained in the synthetic example 10, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 120 weight section, Titanium oxide (Ishihara Sangyo make. TIPAQUE R-820) 20 weight section, DIDP55 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 6500) duplexs, and light stabilizer (the Sankyo make.) SANORU LS7701 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) Tinuvin 3271 weight section, antioxidant (product made from Ouchi Shinko Chemical industry, NOKURAKKU SP) 1 weight section, The amount part of dehydrator vinyltrimetoxysilane (Nippon Unicar make, A-171) duplexs, adhesion grant agent N-beta-(aminoethyl)-gamma-eminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) Three weight sections and the various below-mentioned curing catalysts were added, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained. the neo decanoic acid (the product made from Japan epoxy resin.) which is a non-tin catalyst of the (E) ingredient as a curing catalyst what carried out concomitant use addition of BASA tick 106 weight section and the amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section — working example 19 and isopropoxy titanium bis (ethylacetoacetate) (the Matsumoto Trading make.) What carried out Olga Chicks TC-750 8.5 weight-section addition was made into working example 20. What carried out the amount part addition of dibutyltin bisacatylacetonate (Japanese east transformation make, neo SUTAN U-220) duplexs was made into the comparative example 13.
[0304]
As a result of measuring the recovery by the same method as the above-mentioned using these class products, the hardened material of working example 19 and working example 20 showed the recovery higher than the hardened material of the comparative example 13.
[0305]
(Synthetic example 11)
Use polyoxypropylene glycol of the molecular weight 2,000 [about] as an initiator, and the hydroxyl group end polypropylene oxide of the number average molecular weight 25,500 [about] produced by polymerizing propylene oxide in the zinc hexa cyanocobaltate glyme complex compound catalyst is used, Allyl end polypropylene oxide was obtained in the same procedure as the synthetic example 1. To this allyl end polypropylene oxide, in the same procedure as the synthetic example 1, it was made to react to triethoxysilane and the polyoxyalkylene series polymer (A-11) which has an average of 1.5 triathoxy silyl groups at the end was obtained.
[0306]
(Synthetic example 12)
To the allyl end polypropylene oxide obtained in the synthetic example 11, in the same procedura as the synthetic example 1, it was made to react to methyl dimethoxysilane and the polyoxyalkylene series polymer (A-12) which has an average of 1.5 methyl dimethoxy silyl groups at the end was obtained.
[0307]
(Working example 21 and comparative examples 14-15)
Organic polymer (A-11, A-12) 95 weight section which has the reactive silicon group obtained in the synthetic example 11 and the synthetic example 12, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Toagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section, Zero copy of minute hollow body (the product made from

the Fuji SHIRISHIA chemicals, the FUJIBA luna H-40) which is antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section and the (F) ingredient, or 20 copies were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base rasin. What added 20 copies of minute hollow bodies was made into working example 21, using (A-12) as an organic polymer. What added zero copy of minute hollow body was made into the comparative example 14, using (A-12) as an organic polymer, and what added 20 copies of minute hollow bodies was made into the comparative example 15, using (A-11) as an organic polymer.
[0308]
Using the mixture of 2-ethylhexanoic acid tin (Japanese east transformation make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section as a hardening agent, above-mentioned base resin and hardening agent were mixed uniformly, and workability (********) and endurance were evaluated.
[0309]
The constituent of working example 21 had workability better than the comparative example 14, and its endurance was better than the comparative example 15.
[0310]
(Working example 22 and comparative example 16)
Organic polymer (A-1) 95 weight section which has the reactive silicon group obtained in organic polymer (A-10) 70 weight section which has the reactive silicon group obtained in the synthetic example 10, or the synthetic example 1, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Toagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section, Antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section and the (F) ingredient, or 20 copies were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin. What added 95 copies of (A-1) as an organic polymer was made into the comparative example 16. As a hardening agent, to this base resin, the mixture of 2-ethylhexanoic acid tin (Japanese east transformation make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section was added, and the recovery was measured to it.
[0311]
The constituent of working example 22 showed the recovery higher than the comparative example 16, stooping weight % of an organic polymer low.
[0312]
(Working example 23 and comparative example 17)
Organic polymer (A-10) 95 weight section which has the reactive silicon group obtained in the synthetic example 10, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Toagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section, Antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section and zero copy of epoxy resin (the product made from Japan epoxy resin, Epicoat 828), or five copies were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin. What added five copies of epoxy resins was made into working example 23. What added zero copy of epoxy resin was made into the comparative example 17. As a hardening agent, to this base resin, the mixture of 2-ethylhexanoic acid tin (Japanese east transformation

make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section was added, and the recovery was measured to it.
[0313]
The constituent of working example 23 showed the recovery higher than the comparative example 17.

[0314]
(Working example 24 and comparative example 18)
Organic polymer (A-10) 95 weight section which has the reactive silicon group obtained in the synthetic example 10, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, Hakuenka CCR) 60 weight section, Surface treatment colloid calcium carbonate (product made from Shiraishi industry, BISUKO light R) 60 weight section, Heavy-calcium-carbonate (product made from Shiroishi calcium, HOWAITON SB) 20 weight section, DOP40 weight section, epoxy system plasticizer (New Japan Chemical make, SANSO sizer EP-S) 20 weight section, thixotropic grant agent (made in [Kusumoto Chemicals], DISUPARON 305) 3 weight section, and a photo-setting resin (the Toagosei make.) ARONIKKUSU M-3093 weight section, light stabilizer (Sankyo make, SANORULS770) 1 weight section, Ultraviolet ray absorbent (made in [Tiba Specialty Chemicals], tinuvin 327) 1 weight section and antioxidant (made in [Tiba Specialty Chemicals], IRUGA NOx 1010) 1 weight section were measured, respectively, and it often kneaded with a 3 paint roll, and was considered as base resin.
[0315]
2-ethylhexanoic acid tin (Japanese cast transformation make, U-28) (divalent) 3 weight section and amine (the Wako Pure Chemical Industries make.) lauryl amine 0.75 weight section and dibutyltin bisacetylacetonate (the Japanese cast — transformation — make.) The thing using the mixture of neo SUTAN U-220 0.1 weight section as a hardening agent is made into working example 24, The thing using the mixture of 2-ethylhexanoic acid tin (Japanese cast transformation make, U-28) (divalent) 3 weight section and amine (Wako Pure Chemical Industries make, lauryl amine) 0.75 weight section as a hardening agent was made into the comparative example 18. Base resin and a hardening agent were mixed uniformly and the recovery and thin layer hardenability were evaluated.
[0316]
The constituent of working example 24 showed good thin layer hardenability rather than the comparative example 18, while the high recovery was shown.
[0317]
(Synthetic example 13)
To the allyl end polyisobutylene obtained according to the example of manufacture of JP,H11-209639,A, under existence of Pt catalyst, it was made to react to triethoxysilane and the polyisobutylene (A-13) which has a triethoxy silyl group at the end was obtained.
[0318]
(Synthetic example 14)
To the allyl end polyisobutylene obtained in the synthatic example 13, under existence of Pt catalyst, it was made to react to methyl dimethoxysilane and the polyisobutylene (A-14) which has a methyl dimethoxy silyl group at the end was obtained.
[0319]
(Working example 25 and comparative example 19)
To organic polymer (A-13, A-14) 100 weight section which has the reactive silicon group obtained in the synthetic example 13 and the synthetic example 14, the amount part of dibutyltin bisacetylacetonate (Japanese cast transformation make, neo SUTAN U-220) duplexs was added, and the hardened material was obtained. The thing using (A-13) as an organic polymer was made into working example 25, and the thing using (A-14) was made into the comparative example 19. The hardened material of working example 25 showed the recovery higher than the comparative example 19.
[0320]
(Synthetic example 15)
CuBr (4.2g) and acetonitrile (27.3g) were added to the reaction vessel with an agitator, and it stirred for 15 minutes at 65 ** under a nitrogen atmosphere. Acrylic acid n-butyl (100g), 2, 5-dibromo diethyl adipate (8.8g), and acetonitrile (16.6g) were added to this, and stirring mixing was improved.

Pentamethyl diethylenetriamine (0.17g) was added and the polymerization was made to start. Acrylic acid n-butyl (400g) was dropped continuously, heating and stirring at 70 **. Dividing addition of the triamine (0.68g) was carried out in the middle of dropping of acrylic acid n-butyl.
[0321]
When monomer conversion reaches to 98%, after devolatilizing a ** monomer and acetonitrile at 80 **, 1,7-octadien (53.7g), acetonitrile (132g), and triamine (1.69g) were added, it heated and stirred at 70 ** succeedingly, and the mixture containing the polymer which has an alkenyl group was obtained.
[0322]
Heating devolatilization of acetonitrile in a mixture and the unreacted 1,7-octadien was carried out, and it diluted with the methylcyclohexane. The insoluble polymerization catalyst was made to sediment with a centrifuge, and was removed. Six copies (three copies of KYO word 500SH / 3 copies of KYO word 700SL [:] product [Both] made from Harmony Chemicals) of adsorbent was added to the methylcyclohexane solution of the polymer to 100 copies of polymers, and it heated and stirred under oxygen and nitrogen mixed gas atmosphere. Insoluble matter was removed and the polymer (polymer [P1]) which has an alkenyl group by condensing a polymer solution was obtained.
[0323]
After having carried out heating devolatilization (10 or less torr of decompression degrees), diluting 100 copies of the polymer with 400 copies of methylcyclohexanes further and removing solid content, stirring the obtained polymer [P1] at 180 ** for 12 hours, the solution was condensed and the polymer [P2] was obtained. The number average molecular weight of this polymer [P2] was 24800, and molecular weight distribution was 1.36. The number of the alkanyl groups introduced par one molecule of polymers was 1.8.
[0324]
To this polymer [P2], methyl orthoformate (it is 1 mol equivalent to an alkenyl group), A platinum catalyst (it is 10 mg to 1 kg of polymers as an amount of platinum metal), 1-(2-trimethoxysilyl ethynyl)-1, 1 and 3, and 3-tetramethyl disiloxane (they are 1.5 mol equivalents to an alkenyl group) were added in order, and it mixed, and heated and stirred at 100 ** under a nitrogen atmosphere for 0.5 hour. It checked by ^{1}H-NMR that the alkenyl group had disappeared by a reaction, and the trimethoxysilyl group content polymer (A-15) which condenses a reaction mixture and is made into the purpose was obtained. The number average molecular weight was 27900 and molecular weight distribution was 1.32. The number of the silyl groups introduced par one molecule of polymers was 1.7.
[0325]
(Synthetic example 16)
As opposed to the polymer [P2] obtainad in the synthetic example 15, The triethoxy silyl group content polymer (A-16) was obtained like the synthetic example 15 except having used triethoxysilane (they are 3 mol equivalents to an alkenyl group) instead of 1-(2-trimethoxysilyl ethynyl)-1 used in the synthetic example 15, 1 and 3, and 3-tetramethyl disiloxane. The number average molecular weight was 28600 and molecular weight distribution was 1.48. The number of the silyl groups introduced per one molecule of polymers was 1.5.
[0326]
(Synthetic example 17)
As opposed to the polymer [P2] obtained in the synthetic example 15, It is methyl dimethoxysilane (to an alkenyl group.) instead of 1-(2-trimethoxysilyl ethynyl)-1 used in the synthetic example 15, 1 and 3, and 3-tetramethyl disiloxane. The methyl dimethoxy silyl group content polymer (A-17) was obtained like the synthetic example 15 except having used three mol equivalents. The number average molecular weight was 28400 and molecular weight distribution was 1.51. The number of the silyl groups introduced per one molecule of polymers was 1.5.
[0327]
(Working example 26-28 and comparative example 20)
as opposed to organic polymer 100 weight section which has a reactive silicon group — surface treatment colloid calcium carbonate (the product made from the Shiraishi industry.) Hakuenka CCR150 weight section and heavy calcium carbonate (the Maruo Calcium make.) 25ANANOKKUSU 20 weight section, titanium oxide (Ishihara Sangyo make, TIPAQUE R-820) 10 weight section, DIDP60 weight section, the amount part of thixotropic grant agent (made in [Kusumoto Chemicals],

DISUPARON 6500) duplexs, light stabilizer (Sankyo make, SANORULS765) 1 weight section and an ultraviolet ray absorbent (made in Tiba Specialty Chemicals.) tinuvin 2131 weight section and dehydrator vinyltrimetoxysilane (the Nippon Unicar make.) A-171) the amount part of duplexs, and adhesion grant agent N-beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane (the Nippon Unicar make.) A-1120) Dibutyltin bisacetylacetonate (Japanese east transformation make, neo SUTAN U-220) 0.2 weight section was added as the amount part of duplexs, and a curing catalyst, after kneading in the state where moisture does not exist substantially under drying conditions, it sealed in the dampproof container and 1 liquid mold-curing nature constituent was obtained. The **** thing for 100 weight sections is made into working example 26 for the acrylic ester system polymer (A-15) which has the trimethoxysilyl group obtained in the synthetic example 15 as an organic polymer which has a reactive silicon group. (A-15) Make the **** thing for a total of 100 weight sections into working example 27 for the mixture of 50 weight sections and polyoxyalkylene series polymer (A-4) 50 weight section which has the methyl dimethoxy silyl group obtained in the synthetic example 4, The **** thing for 100 weight sections is made into working example 28 for the acrylic ester system polymer (A-16) which has the triethoxy silyl group obtained in the synthetic example 16, The **** thing for 100 weight sections was made into the comparative example 20 for the acrylic ester system polymer (A-17) which has the methyl dimethoxy silyl group obtained in the synthetic example 17. The hardened material of working example 26-28 showed the recovery higher than the comparative example 20.

[Industrial applicability]

[0328]

Tha hardenability constituent of this invention is excellent in stability, endurance, and creep resistance.

[Translation done.]